

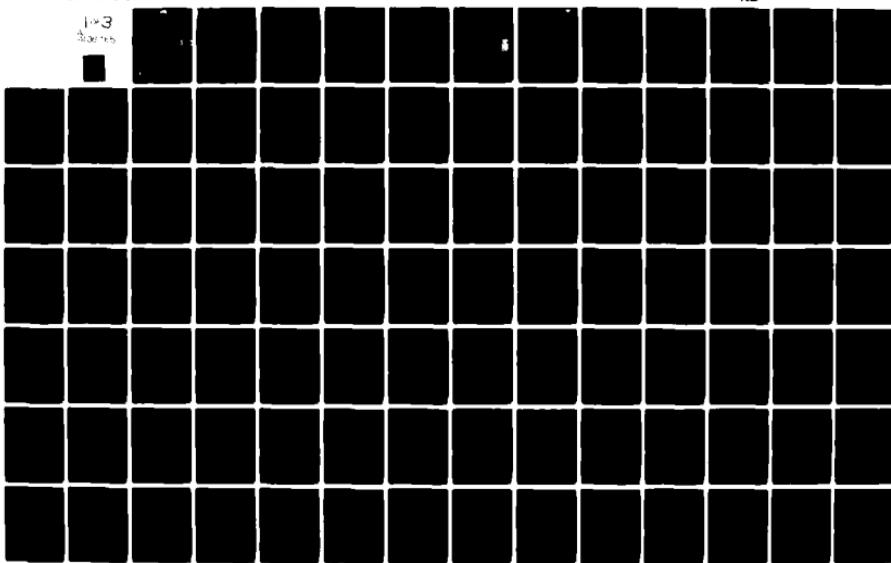
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Larson, Jay Leo (Ph.D., Geology)

A Study of the Diffusion, Electrochemical Mobility and Removal of Dissolved Copper in a Saturated Porous Medium

Thesis directed by Professor Donald D. Runnels

The purpose of this study was to determine if the migration and removal of dissolved copper in a saturated porous medium could be controlled electrochemically with an acceptable expenditure of electrical current. The theoretical discussion attempted to provide a complete survey of the factors which affect the movement and removal of metal ions in a saturated porous medium using electrochemistry. Some of these factors did not apply to the experimental work performed in this study, but they were discussed because of their possible effects on the field utilization of the proposed electrochemical technique of pollution control.

A series of experiments were performed to demonstrate the relationship between passive Eh and induced EMF as they are used in this study. Using two platinum electrodes with a constant direct current potential induced between them, it was shown that the voltage of each individual electrode could be measured relative to a reference electrode. The voltage of the individual platinum electrode relative to the reference appeared to be a function of the type of solute, the concentration of the solute, and distance between the platinum and reference electrodes.

A laboratory technique for studying ionic transport, called the "frozen tube method," was developed specifically for this stu

11

A cylindrical acrylic tube was filled with quartz sand saturated with an aqueous solution of copper sulfate. The processes of ionic transport, either naturally or electrochemically activated, were allowed to occur for a set amount of time. The experimental run was terminated by immersing the tube in liquid nitrogen to halt the processes of ionic transport in time and space. While the tube was still frozen, it was sliced into sections. When the sections had thawed, the contents of each were analyzed. The analyses of each section provided information about the ionic migration within the tube.

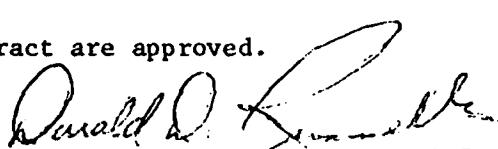
It was demonstrated that the frozen tube method could produce basic data about diffusion. After the diffusion of cupric ions through the interstitial fluid which filled the pore spaces of a pure quartz sand with a porosity of 34% was allowed to proceed for 15 days, the frozen tube method was used to record the concentration-distance curve. An apparent diffusion coefficient for cupric ion was calculated graphically from the concentration-distance curve; the value was $0.69 \times 10^{-5} \text{ cm}^2/\text{sec.}$

The frozen tube method was used to study the electrochemical removal of dissolved copper from a solution saturating the pore spaces of a quartz sand. Platinum electrodes were installed at each end of the tube and a direct current potential was induced between the electrodes. Removal of dissolved copper was accomplished by reduction of the ions to the native state at the surface of the cathode. The variables which were tested were time, pH and the background matrix of the solution. In this stagnant encapsulated

system, 23% of the total copper was removed in three days but only 52% was removed in thirty days from a solution containing 617 ppm dissolved copper. As pH of the starting solution containing 615 ppm copper was decreased from 4.0 to 2.0, the current efficiency of reducing copper decreased from 76% to 4%. A solution containing a background matrix of groundwater components and 59 ppm dissolved copper from a total dissolved solids concentration of 736 ppm was tested; 25% of the total dissolved copper was removed in five days with a current efficiency of 9%. This study concluded that this electrochemical technique may be feasible for pollution control in some field settings.

The form and content of this abstract are approved.
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Signed


Donald D. Ritter
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A STUDY OF THE DIFFUSION, ELECTROCHEMICAL MOBILITY AND
REMOVAL OF DISSOLVED COPPER IN A SATURATED POROUS MEDIUM

by

Jay Leo Larson

B.S., Iowa State University, 1967

M.S., South Dakota School of Mines, 1971

A thesis submitted to the
Faculty of the Graduate School of the
University of Colorado in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
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1980

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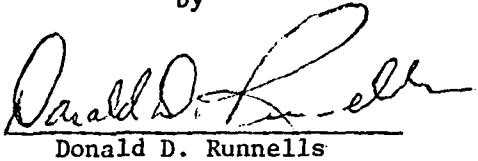
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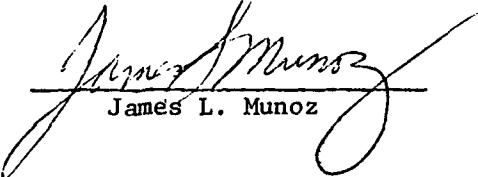
by



Donald D. Runnels



Bruce F. Curtis



James L. Munoz

Date Nov. 11, 1980

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CHAPTER 1

INTRODUCTION

1-1. Purpose and Application

Pollution of his environment has become one of man's greatest problems, and techniques for effective prevention and rehabilitation of these man-made hazards are in great demand. This project was undertaken in an attempt to develop a technique for mitigation of environmental hazards due to releases of heavy metals in the ionic form. An example of a specific type of problem envisioned here would be a fairly small area of land highly contaminated with dissolved metals. Many such areas undoubtedly exist throughout the world.

The general work described here utilizes a combination of electrochemical phenomena. The specific technique consists of inserting metallic electrodes in the contaminated medium and applying a low voltage, direct-current between the electrodes. Three electrochemical phenomena may operate together to remove the contamination: (1) reduction of metallic cations to the native state at the cathode, (2) subsequent diffusion of additional cations toward the cathode resulting from the concentration gradient caused by reduction, and (3) normal ionic migration under the influence of the electrical field. Obviously, sufficient water must be present in the porous medium for these mechanisms to operate, and this factor will be discussed. In some circumstances, water may be added to the contaminated ground. The technique developed by this study

requires the blending of the science and technologies of physical chemistry, electrochemistry, electroplating, and geohydrology.

It was hoped at the outset of this project that the electrochemical technique would prove economical for field use, but it is extremely difficult to define what is economical where the environment is concerned. The end-point of the projected cleanup is reached when the concentration of the contaminant is at a value which is below the environmentally hazardous level, or is so low as to be economically unfeasible for further removal. Such determinations, of course, are dependent on the relative toxicity of the contaminant, the restrictions imposed by regulatory agencies, and the cost of the cleanup. A method for calculating costs will be discussed in Section 5-2-5.

One great advantage in using the proposed type of electrochemical procedure is that cleanup can be accomplished in situ. This means that it can be accomplished with minimum disruption to the site. Further, once the cleanup is finished the problem is truly solved because the contaminant will have been concentrated and recovered, not merely transferred in dilute form to another location. For example, if a contaminated soil were to be removed, the problem of disposal would still remain. Similarly, if the soil were to be flushed with fresh water, a large volume of dispersed contaminated liquid would still have to be disposed.

The nature of the technique inherently restricts its use. It may be most usefully applied to fairly small parcels of land,

perhaps ten acres or less; in special circumstances, larger areas of contamination may be considered. Another limiting factor in the practical use of electrochemical cleanup is the depth of contamination; it should be no more than a few tens of feet deep, or if the contamination is deep in the subsurface, it should be confined to a vertical thickness of a few tens of feet. The experimental work conducted in this study simulated contamination in a stagnant situation, but the application of electrochemical cleanup to water moving very slowly in an aquifer is also considered.

The work reported here utilizes dissolved copper as the experimental contaminant. The reasons for using copper for experimental work are many. The literature on copper is extensive in all of the technical fields involved in the project. Copper is also easy to handle in the laboratory; it is readily available, inexpensive, and relatively non-toxic.

In some field situations, copper itself may be a pollutant, and the methods devised here could be used directly in field cleanup. Moore and Moore (1976) list copper as one of the most ubiquitous of the heavy metals contained in effluents from various industries. Mining operations may be one of the greatest contributors of dissolved copper into the environment. Galbraith and others (1972) discuss the mechanism by which metal ions are leached by water passing through mine tailings. Simply, the oxidation of sulfide increases the hydrogen ion and sulfate ion concentrations, and metal ions go into solution as metal sulfates. Rubin (1974) shows

that copper concentrations as high as 100 mg/liter have been recorded in rivers receiving acid mine drainage, specifically the Kiskimimitas River at Apollo, Pennsylvania. The Public Health Service standard for copper in drinking water is one milligram per liter, but this is based on taste and not potential toxicity (U.S. Public Health Service, 1962). As a by-product of this study, the method may have a commercial application for the recovery of copper from such areas as mine tailings deposits.

Although copper was used to develop the technique, there are possible analogous applications for the toxic heavy metals such as cadmium, chromium, lead, and others. The feasibility of using the electrochemical technique to remove metals other than copper from solution has been demonstrated by the electroplating industry which commercially reduces a wide spectrum of metals from solution to the native state. Chromium is unique in this brief list of metals given above because it is present in the plating bath primarily as an anionic complex. Chromium can be electroplated from an aqueous solution of chromic acid. Both the $(\text{HCrO}_4)^-$ ion and the $(\text{HCr}_2\text{O}_7)^-$ are more abundant than the Cr^{3+} ion in chromic acid solutions (Raub and Müller, 1967). It is also possible to electroplate arsenic and selenium out of aqueous solutions in which the metals are present as anionic complexes (Holt, 1974). The presence of metals in solution as anionic complexes would complicate the mechanisms of ionic transport beyond what is reported in this study. Therefore, such metals will not be discussed in detail.

1-2. Previous Work

The use of electrochemistry as an environmental tool is a relatively new area of study. One of the most comprehensive treatments of the general subject was done by Bockris (1972) in his book "Electrochemistry of Cleaner Environments", but it contained nothing remotely similar to the work performed in this study. The work of Kuhn (1972) comes closer to the type of problem being dealt with here; he surveys the electrochemical methods which can be used to clean up aqueous effluent. One important process discussed by Kuhn (1972) is the reaction which occurs at the anode, such as the anodic decomposition of cyanide. Anodic processes will be explored in this paper because in some cases the use of electrochemical cleanup may do double service. However, to the best of my knowledge, the use of electrochemistry to clean up a pollution problem in situ has not previously been published.

Some aspects of aqueous chemistry, applicable to this study, have been researched in detail. Great volumes of published literature are available on diffusion, diffusion coefficients, ionic mobility, electroplating, and so on. The method of studying diffusion called the diaphragm cell method can, in some respects, be considered a predecessor of the work performed in this study. In this approach two test solutions are separated by a porous membrane, and the rate of diffusion through the membrane is measured. Gordon (1945) discussed the development and use of the diaphragm cell method for studying the phenomenon of diffusion prior to 1945. Stokes (1950) discussed the effects of some of the

obvious variables on results obtained using the stirred, porous diaphragm cell, and later he (Stokes, 1951) showed how to calibrate such a cell for general use in diffusion studies. The experimental technique used in this study recommends a calibration procedure analogous to that described by Stokes. The diaphragm cell method is still a primary technique for gathering data on diffusion. Of interest to this study is the recent paper by Woolf and Hoveling (1970) in which they published data on diffusion coefficients of copper sulfate.

The literature on diffusion in geological materials is somewhat sparse. Garrels and others (1949) performed some of the first good definitive experimental work on diffusion of dissolved substances through the pore spaces in rocks. Garrels' team used a diaphragm cell designed after the one described by Gordon (1945). They utilized a thin wafer of limestone as the diaphragm and measured the diffusion of potassium chloride through the limestone. They showed that diffusion could be a major mechanism for the transfer of dissolved materials in the subsurface. Some of the more recent authors, such as Golubev and Garibyants (1971), take a mathematical approach to the problem of diffusion in rocks. Various aspects of diffusion in soils and sediments have also been studied by others (Klinkenberg, 1951; Lai and Mortland, 1961; Dutt and Low, 1962; Manheim, 1970; Duursma and Hoede, 1976). This present study combines techniques and theories to produce a new and useful laboratory procedure and, hopefully, environmental tool.

1-3. Method of Study

Laboratory work was directed toward two goals: (1) determining the feasibility of using an electrochemical technique to remove dissolved copper from an aqueous solution saturating a porous medium and (2) producing basic data concerning the movement of copper ions through a saturated porous medium. The first step was to find a laboratory technique which would satisfy the goals of the project. A variety of methods of study were attempted; these included column experiments and a variation of the diaphragm cell method in which electrodes were inserted into the test solutions, one on each side of the membrane. As experimentation progressed it became clear that valuable information could be gained if the processes of ionic transport could be halted in time and space. This thought led to the development of a new experimental technique.

The new technique developed in this study became the primary method of studying ionic transport in a saturated porous medium. The technique will be referred to as the frozen tube method. The frozen tube method halts ionic transport in time and space by instantly freezing the test solution. The method consists of packing a plastic tube with a porous material which is saturated with a solution of dissolved copper. Electrodes may be introduced at each end of the tube so that a direct electrical current can be passed through the tube. At the end of an experiment, the tube is immersed in liquid nitrogen to freeze the solution as rapidly as possible. The rapid freezing stops all processes of ionic

transport at an instant in time and space. The tube is physically sliced into sections of equal length while still frozen. Each section is allowed to thaw, and its interstitial fluid can then be analyzed for its concentration of dissolved copper, sulfate ions, and hydrogen ions. The analysis renders the average concentration in each section, but it shows differences along the length of the tube. In this way a concentration gradient can be recorded. The data derived from frozen tube experiments satisfied both of the goals of the laboratory phase of this project. The frozen tube method is a new tool offering great potential for investigating the mechanisms of ionic transport, and possibly other geochemical phenomena, in both natural and laboratory materials.

CHAPTER 2

THEORY

2-1. Introduction

In order to study the movement of dissolved metals in a saturated porous medium, we must first examine the parameters which affect this movement. These parameters are the nature of the porous medium itself, the interstitial fluid, and the geochemical conditions. Each parameter will be considered separately, but as each is discussed their interrelated nature should become obvious.

This chapter is intended to be a complete survey of the factors which affect ionic transport. Therefore, some of these factors do not apply to the specific conditions created in the laboratory phase of this project. This chapter was compiled in order to give the reader an appreciation for the complexities of ionic transport in a saturated porous medium. It may also assist future researchers in applying this work to other environments.

2-2. Porous Medium

Two important physical properties of a porous medium are porosity and permeability. Porosity, ϕ , is a dimensionless term defined as the volume of void space, V_v , divided by the volume of bulk space, V_b , occupied by the porous medium.

$$\phi = V_v/V_b \quad (2-1)$$

Porosity alone cannot be used as a measure of the amount of material which may pass through a porous medium; for example, in an extreme case the voids in a porous medium may all be isolated cells which are not interconnected. Permeability, on the other hand, is a measure of the ability of a porous medium to transmit fluid through it.

2-2-1. Permeability and Porosity

Permeability is determined by measuring the amount of discharge of fluid per unit time from a porous medium under the existing conditions. Todd (1959, p. 52) gives the following formula for permeability:

$$k = \frac{\eta Q/A}{w(dh/dL)} \quad (2-2)$$

where k = permeability (darcys)

η = viscosity of the fluid (centipoises)

Q = discharge of the fluid (cm^3/sec)

A = cross sectional area of the porous medium (cm^2)

w = dimensionless specific weight of the fluid

dh/dL = change in head per unit length of porous medium
(atm/cm).

Conversion factors can be used to change the units to other systems such as the cgs system, but the darcy is the most commonly used unit for permeability.

Although permeability is considered a basic measurement of a porous medium, Bear (1972) says that permeability is actually

dependent on three more elementary properties of the porous medium: porosity, average medium conductance, and average tortuosity. Bear states that average medium conductance is related to the cross-sections of the elementary channels through which flow takes place, but he gives no relationship between the two. However, as we further explore the parameters required for this study, it will be shown that we do not need the term of average medium conductance.

Permeability is an applicable measurement in all cases where the fluid is in motion in the porous medium, but in the experimental situation discussed in this report, the dissolved ions are in motion in a static fluid. In the work of Garrels and others (1949) on diffusion of ions in a saturated porous medium, they examined the parameters which affect the rate of diffusion and the quantity of ions transferred. They concluded that the rate of advancement of ions is independent of permeability or bulk porosity of the medium, but that the amount of material transferred depends upon the effective directional porosity. The fact that permeability is not a controlling parameter in ionic diffusion is the reason why we need not use the concept (Bear, 1972) of average medium conductance.

Bear (1972) defines effective porosity, ϕ_e , as the ratio of the interconnected pore volume, $(V_v)_e$, to the total volume of the medium, V_b .

$$\phi_e = (V_v)_e / V_b \quad (2-3)$$

Effective porosity is an important term when the porous medium contains a large number of dead end pores. In an unconsolidated medium, effective porosity, ϕ_e , equals volumetric porosity, ϕ .

2-2-2. Tortuosity

When diffusion takes place in a fluid in the pore spaces of a porous medium, the basic diffusion equation for a bulk fluid must be altered to account for the presence and effect of the porous medium. In the simplest case the porous medium is inert, and there is no chemical or physical interaction between the constituents of the fluid and the porous medium. Bear (1972) gives the following formulas for diffusion in this situation. First, molecular diffusion in a homogeneous liquid can be expressed by Fick's first law:

$$J = -D \text{ grad } C \quad (2-4)$$

where J = molecular flux

D = diffusion coefficient

$\text{grad } C$ = concentration gradient.

If the same liquid saturates a porous solid medium, the molecular flux per unit area of porous medium becomes:

$$J^* = -\phi D T \text{ grad } C = -\phi D^* \text{ grad } C \quad (2-5)$$

where J^* = molecular flux per unit area of porous medium

ϕ = porosity

T = tortuosity

D^* = diffusion coefficient in the porous medium.

Tortuosity, T , is defined as the ratio of the diffusion coefficient in the porous medium, D^* , to the diffusion coefficient in the bulk liquid, D .

$$T = D^*/D \quad (2-6)$$

Tortuosity is also a parameter which affects the electrical conductivity of an electrolytic fluid in a medium. Ohm's law of electricity states that:

$$i = -K \text{ grad } E \quad (2-7)$$

where i = electrical flux

K = electrical conductivity

$\text{grad } E$ = gradient of electrical potential.

If the same electrolyte saturates an inert, non-conductive, porous medium, Bear (1972) changes Ohm's law to:

$$i^* = -\phi K T \text{ grad } E \quad (2-8)$$

where i^* = electrical flux per unit area of porous medium

ϕ = porosity

T = tortuosity.

Tortuosity is clearly an important parameter. It will be helpful to look at the background and definition of this term.

The concept of tortuosity comes from work that was done in the field of chemical engineering. Carman (1937) derived an equation for the velocity of a fluid passing through a bed of unconsolidated spherical particles. The equation given by Carman

(1937, p. 152) is:

$$v = \frac{\phi m^2}{k_o \eta} \cdot \frac{\Delta P g}{L} \left(\frac{L}{L_e} \right)^2 \quad (2-9)$$

where v = apparent velocity of fluid (cm/sec)

ϕ = porosity (dimensionless)

m = mean hydraulic radius (cm)

k_o = constant for streamline motion through channels
of uniform cross section; for circular sections,

$k_o = 2.0$

η = viscosity of fluid (poises)

ΔP = pressure difference across bed of length L
(grams/cm²)

g = acceleration due to gravity (cm/sec²)

L = length of bed in direction of flow (cm)

L_e = actual length of path taken by fluid in traversing
bed of length L (cm).

Although Carman (1937) never used the term tortuosity, he did refer to the ratio L_e/L as the correcting factor necessary in the velocity equation. Carman (1937) suggested that the numerical value of $L_e/L = \sqrt{2}$ was reasonable based on his own experiments.

The ratio of length of flow path to the length of the sample of porous medium is a concept readily understandable in physical terms, and it is from this ratio that we get the term of tortuosity. Collins (1976) uses the simple ratio to define tortuosity. Bear (1972) prefers to define tortuosity as follows:

$$T = (L/L_e)^2. \quad (2-10)$$

This controversy over definition need not be resolved here, for it deals with a definition based on fluid in a dynamic state. For the purpose of this study, Bear's use of tortuosity for a static fluid will be satisfactory.

2-3. Interstitial Fluid

The interstitial fluid is the fluid contained in the voids of the porous matrix. The interstitial fluid in most natural situations is water. The conditions of the interstitial fluid will be examined in detail, and it will be shown how these conditions affect the application of the electrochemical technique for environmental clean-up in the field.

2-3-1. Fluid Movement

The movement of the interstitial fluid in a porous medium will affect the removal of dissolved metals. A static system would be theoretically most easy to consider. The laboratory work performed for this study used a static fluid model. However, groundwater is almost always in a state of motion, so the static model would probably limit our understanding and predictions to natural situations in which the rate of flow of the groundwater is very slow.

A field situation where the interstitial fluid is in motion is not necessarily beyond the scope of this technique. In fact, a slow rate of flow could not only be tolerated but could be helpful to the efficient removal of dissolved metal ions. For a slow

rate of flow to assist in metal removal, the cathode should be positioned downstream from the anode. It will be shown in the experimental section that a slow rate of fluid flow would assist the geochemical and electrochemical mechanisms in transporting dissolved metal ions to the cathode. A rate of flow of fluid considered slow enough to be useful would be a velocity measured in terms of centimeters per day. The problem with a more rapid rate of flow is that the velocity of the fluid exceeds the rate of removal by reduction, and only a very small fraction of the metal is removed as the fluid passes the cathode.

2-3-2. Degree of Saturation

The degree of saturation is a practical consideration based on the effective removal of ions from the fluid. In general, the porous medium should be saturated with fluid. Golubev and Garibyants (1972) state that the diffusion coefficient declines with a decrease in the moisture content in rock. Since diffusion is a contributing mechanism for driving the dissolved metal toward the cathode, anything which decreases diffusion will decrease the rate of removal of metal. Regardless of the mechanism, however, the interstitial fluid is the transport medium in which the ions move. Some field conditions, such as near-surface, unsaturated soils, may be improved for cleanup by adding water from an external source in order to increase the degree of saturation.

2-3-3. Applied Potential

The interstitial fluid is one of the factors which controls the potential applied between two electrodes by the power supply. The applied voltage must be below the value at which water decomposes into its elemental gases, hydrogen and oxygen. However, in order to reduce dissolved metals from solution as rapidly as possible, the voltage should be set as high as possible without causing the decomposition of water. The applied potential will, in most cases, be between two and three volts. If gas bubbles are produced at the electrode surfaces, the decomposition of water will reduce the rate of metal removal from the interstitial fluid due to several effects. These include: (1) reducing the degree of saturation of the porous medium, (2) increasing the tortuosity in the porous medium, and (3) reducing the effective surface area of the electrodes. However, there is also an economic advantage in applying less than three volts of potential, and that is cost. The relationship between applied potential and direct current and cost will be discussed later.

2-4. Geochemical Conditions

The geochemical conditions are also variables of interest in this study. The parameters previously discussed are generally fixed by field conditions so their effects upon ionic transport are relatively simple. The list of geochemical conditions which can affect ionic transport in the system under study is quite extensive.

Most of the geochemical conditions are subject to variation during the process of removing dissolved metal from solution. It is the change in geochemical conditions which makes their effect upon ionic transport more complex to study.

Generally, the geochemical conditions of an environment are natural, but in this study we will also examine conditions artificially imposed on the system by the electrodes. The natural conditions of the solvent and the solute and possible reactions with the substrate will be discussed before the electrochemical parameters.

2-4-1. Solvent

The term of solvent is used in this study to mean the interstitial fluid contained in the porous medium. The only solvent considered in this study is water. The three most commonly measured variables in an aqueous system are Eh, pH, and temperature. The Eh and pH are important to this study because they control the distribution of ionic species contained in the solvent.

2-4-1-1. Eh

Eh is a very broadly used and accepted measurement, but its definition is slightly elusive. Langmuir (1971) says that Eh is a measure of the aqueous electron concentration. Garrels and Christ (1965), on the other hand, call Eh the oxidation potential of a half cell referenced to a standard hydrogen half cell. The latter definition connotes that Eh measures the Nernst potential of a

half cell reaction such as



This is, in fact, possible if an electrode composed purely of the same metal as that in solution is used in conjunction with a reference electrode. However, this is usually not the case under the conditions used for routine Eh measurements. Eh is measured with a pair of electrodes, an inert electrode and a reference electrode of convenience. The Nernst potential is not observed with this pair of electrodes because the inert electrode does not participate in a reaction as a copper electrode would in the reaction shown in Equation (2-11).

The inert electrode is usually bright platinum, and the reference electrode is commonly a saturated calomel electrode. The calomel electrode consists of mercury in contact with mercurous chloride which is in turn in contact with a saturated solution of potassium chloride. At 25°C , the value of Eh for the saturated calomel electrode is +0.2444 volt relative to the standard hydrogen electrode (Garrels and Christ, 1965). The observed potential between the platinum and the reference electrodes is actually an EMF reading, and this voltage must be corrected by the magnitude of the voltage of the reference electrode in order to calculate a true Eh relative to the standard hydrogen electrode.

In spite of the fact that different authors approach the concept of Eh differently, certain generalizations can be made about the readings of Eh as taken with an electrode pair. Aqueous

systems which contain dissolved oxygen or similar oxidizing agents will usually give positive Eh values and reducing systems will usually give negative values (Morris and Stumm, 1967). As a result of my work, however, I agree with Morris and Stumm (1967) about the questionable value of detailed quantitative interpretation of Eh readings; equilibrium is often in doubt and in most natural systems Eh measurements must represent undefined mixed potentials. The value of Eh readings is based more upon laboratory studies where measurements can be made on simplified systems.

2-4-1-2. pH

The pH is a precisely defined parameter of great importance in all areas of geochemistry. The numerical value of pH is defined as the negative logarithm of the hydrogen ion activity (Garrels and Christ, 1965). Because ion activity can be measured directly by electrode, pH is measured by a glass electrode in combination with a reference electrode, usually calomel. The importance stems from its relationship, and in some cases control, of other geochemical parameters.

In the first place, the concentration of dissolved metals in solution may be controlled by pH because of its effect on the solubility of many minerals. In the copper system, pH controls the solubility of cupric oxide and hydroxy-carbonate minerals. Hem (1970) believes that this solubility control limits the concentration of dissolved copper in aerated waters to 64 micrograms/liter at pH 7.0 and to 6.4 micrograms/liter at pH 8.0. Conversely, at

low values of pH, the concentration of dissolved copper can be quite high. Hem (1970) lists the case of an acid water draining from a copper mine in Ducktown, Tennessee which contained 312 milligrams/liter of dissolved copper. In this study, test solutions were used which contained 620 milligrams/liter copper at pH 4.5.

Once a metal is in solution, pH may still control factors of interest to this study. The pH is known to influence such factors as the distribution of ionic species, adsorption of ions on a substrate, electrodeposition, etc. The distribution of ionic species is commonly expressed as a function of both pH and Eh. This, however, depends upon the system of interest: some systems are pH dependent, some are Eh dependent, and others are controlled by both. Adsorption and electrodeposition are functions which may be directly affected by the pH of the solution. All of these relationships will be discussed later.

2-4-1-3. Temperature

Temperature is another variable of concern. Temperature is an intensive property which may greatly affect the state of the system. Because temperature is related to the internal energy of the system, it is one of the important parameters which controls the movement of ions.

2-4-2. Solute

The solute is the substance dissolved in a solution; in the case of this study, the solute is dissolved copper. The ability to remove dissolved copper from a solution is affected by several conditions of the solute. The geochemical conditions of the solute

that will be discussed are the parameters of concentration and concentration gradient and the intrinsic conditions of diffusion coefficient, distribution of ionic species, and complexing. It will be shown how these conditions affect the transport mechanisms of diffusion and ionic mobility. This discussion assumes that the solution itself is static unless otherwise stated.

2-4-2-1. Concentration

The concentration of an electrolytic solute in solution affects both mechanisms of ionic transport of interest in this study. The way in which we see that concentration affects diffusion is by looking at the diffusion coefficient. The basic mathematical expression for diffusion is Fick's first law of diffusion named after Fick who saw an analogy between molecular diffusion and the conduction of heat (Crank, 1957). Fick's first law is expressed as:

$$J = -D \frac{\partial C}{\partial x} \quad (2-12)$$

where J = molecular flux per unit area of section

(moles/cm² sec)

D = diffusion coefficient (cm²/sec)

$\frac{\partial C}{\partial x}$ = concentration gradient measured perpendicular to the section (moles cm⁻³/cm).

Diffusion coefficient is a parameter which is dependent upon the concentration of the solute; the values of diffusion coefficient increase as the concentration decreases (Woolf and Hoveling, 1970).

From Equation (2-12) it can, therefore, be seen how concentration affects ionic transport through the diffusion coefficient.

Diffusion coefficients will be discussed in more detail in Section 2-4-2-3.

Concentration also affects the mechanism of ionic mobility. This can be seen directly because there is a concentration term in the equation for ionic flux resulting from an electrical potential (Bockris and Reddy, 1970).

$$(J_c)_i = u_i C_i \frac{\partial E}{\partial x} \quad (2-13)$$

where $(J_c)_i$ = ionic flux (moles/cm² sec)

u_i = ionic mobility (cm sec⁻¹/volt cm⁻¹)

C_i = concentration (moles/cm³)

$\partial E / \partial x$ = electrical potential gradient (volts/cm):

Ionic mobility will be discussed in greater detail in Section 2-4-4-4 along with the other electrochemical parameters.

2-4-2-2. Concentration Gradient

A concentration gradient exists whenever different concentrations of a solute are present in separated areas of a single fluid. It is called a gradient because some type of gradational change between the areas of greatest concentration difference always exists. There are many examples of concentration gradients existing in nature where dissimilar waters come in contact with each other (Runnels, 1969). A concentration gradient can also be artificially created. The use of the electrochemical technique will create a

concentration gradient by decreasing the concentration of dissolved metal in the area of the cathode where dissolved metals will be reduced to solids. Regardless of the cause of a concentration gradient, the mechanisms of diffusion and, in some cases, osmosis operate to eliminate the gradient. It is the effect of a concentration gradient on these mechanisms which is of interest to this study.

2-4-2-2-1. Diffusion

The effect of concentration gradient on the mechanism of diffusion is easily shown by the basic equations for diffusion. The first law of diffusion was already shown in Equation (2-12) which is repeated here.

$$J = -D \frac{\partial C}{\partial x} \quad (2-12)$$

This equation represents one dimensional diffusion but can be easily modified for three dimensions. Fick's first law defines a steady state condition; in other words, the concentration gradient $\partial C / \partial x$ remains constant with time. Another requirement for the first law of diffusion to be valid is that the concentration gradient must be linear.

Fick's second law of diffusion, which deals with the nonsteady state condition, is:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (2-14)$$

where C = concentration (moles/cm³)

t = time (sec)

D = diffusion coefficient (cm²/sec)

x = distance (cm).

In the situation defined by the second law of diffusion, the concentration gradient is not linear.

From these simple equations are derived the complex equations which must be used to simulate conditions found in nature, such as three dimensional diffusion in an anisotropic medium. Crank's (1957) entire book on the mathematics of diffusion deals with the modification of these equations to suit different conditions and different geometrics confining the medium.

The mechanism of diffusion is responsible for an electro-chemical phenomenon called diffusion potential which is of interest to this study. Lakshminarayanaiah (1969) describes a concentration cell with transference which is very similar in design to the laboratory apparatus used here for frozen tube experiments. A diagram of the concentration cell is shown in Figure 2-1.

Direct transference of electrolyte from the area of higher concentration to the area of lower concentration takes place indicated on the diagram in Figure 2-1. The result of the transfer of ions is the establishment of an electrical potential across the cell called a diffusion potential. Assuming this is a simple system with a single univalent electrolyte, the diffusion potential across the cell is given by the following equation

(Lakshminarayanaiah, 1969, p. 69):

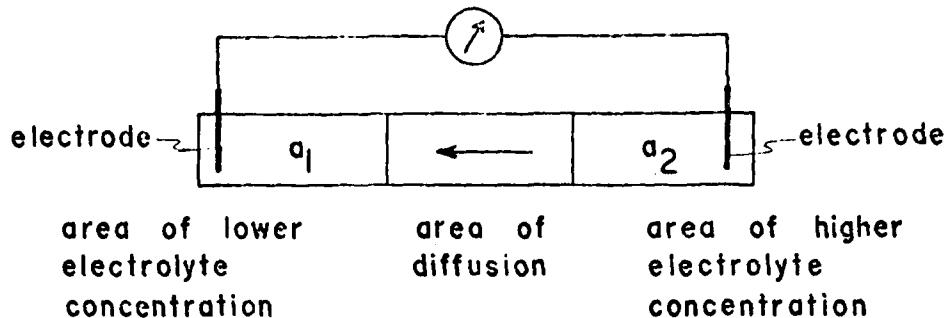


Figure 2-1. Concentration cell with transference.

$$D = t_- \frac{2RT}{F} \ln \frac{a_2}{a_1} \quad (2-15)$$

where E = electrical potential (volts)

t_- = transference number of the anion (dimensionless)

R = ideal gas constant (1.987 cal/deg mole)

T = temperature (degrees K)

F = Faraday's constant (23,062 cal/volt equiv)

a_2 = activity of the electrolyte in concentrated side (moles/liter)

a_1 = activity of the electrolyte in dilute side (moles/liter).

Lakshminarayanaiah (1969) chooses the transference number of the anion arbitrarily and assumes that it is equal to the transference number for the cation.

Bockris and Reddy (1970) improved Equation (2-15) by accounting for the individual characteristics of the anion and the cation and allowing for multivalent ions. Their equation for diffusion

potential is shown below (Bockris and Reddy, 1970, p. 416).

$$E = \frac{RT}{F} \sum \frac{t_i}{z_i} d \ln a_i \quad (2-16)$$

where t_i = transference number of ion i (dimensionless)

z_i = valence of ion i (equiv/mole)

a_i = activity of ion i (moles/liter).

In the case of the frozen tube experiments where a voltage is applied across the cell, the cathode is located in the area of lower electrolyte concentration, and the anode is located in the area of higher electrolyte concentration. The diffusion potential will oppose the applied potential, but this does not create a problem for the frozen tube experiments. Using Equation (2-16), the maximum possible diffusion potential would be -0.015 volt, whereas the applied potential is +2.50 volts.

2-4-2-2-2. Osmosis

Osmosis, like diffusion, is a mechanism of chemical transport driven by a concentration gradient. Unlike diffusion, osmosis is the flow of the solvent, not the solute. If two solutions of different solute concentrations are separated by a semi-permeable membrane, the solvent will flow through the membrane from the dilute solution to the concentrated solution, reducing the concentration gradient. The osmotic process will proceed whether the dissolved substance is an electrolyte or a non-electrolyte. Osmosis may be prevented by applying a counter-balancing pressure to the more concentrated solution. The amount of pressure required to prevent the flow of fluid is called the osmotic pressure (Collins, 1976).

Ultimately, osmosis should proceed until the concentration of the two solutions approaches equality, or until a hydrostatic pressure develops on the concentrated side. If there is a hydrostatic pressure build-up in the concentrated solution, osmosis will stop when the hydrostatic pressure equals the osmotic pressure (Glasstone, 1940).

There are many types of materials which act as semi-permeable membranes. Biological materials which act as membranes function with varying degrees of osmotic efficiency. For example, such animal membranes as the wall of a bladder are not as efficient as the plasma membrane in the wall of a plant cell (Glasstone, 1940). More to the point of this study, some geological materials, particularly compacted clays and shales, behave as semi-permeable membranes (Collins, 1976). In fact, some of the early attempts to quantitize the effects of osmosis were made using membranes prepared from natural clays (Morse, 1914). However, the most efficient osmotic membranes which are now synthetically produced for commercial applications are made from organic polymers (Lakshminarayanaiah, 1969).

The reason that osmosis must be considered in this study is that it is a phenomenon which could reduce the efficiency of the electrochemical technique of cleanup. In a clay-rich geological environment, osmosis would act as a competing mechanism to electrochemical and chemical diffusion. In the proposed technique, as a concentration gradient is created between the electrodes, osmosis will impede the flow of ions by establishing a flow of water in the direction opposite to the desired gradient in concentration.

Osmosis, like diffusion, is associated with an electrochemical phenomenon. In this case the phenomenon is known as electro-osmosis. Osmosis and electro-osmosis may be associated more by name than by function. Bockris and Reddy (1970, p. 826) graphically explain electro-osmosis with the diagram shown in Figure 2-2. When an electrical potential is applied to an electrolyte solution in a capillary tube, the solution itself starts to flow as well as a flow of electrical current. This phenomenon also occurs when the electrodes are separated by a membrane, or it may occur in a soil or clay with relatively small pore spaces. Electro-osmosis apparently results from the relative difference in resistance of the solvent toward the two charged species as they migrate toward the electrodes (Lakshminarayanaiah, 1969). The direction of solvent movement is usually toward the cathode because the hydrated radius of most cations is larger than that of anions (Nightingale, 1959). Judging from the mechanism of electro-osmosis, it is understandable that its effect is minuscule, but that effect would generally favor the transport of ions toward the cathode.

In the absence of a hydraulic pressure gradient, but in the presence of an electrode pair, Bockris and Reddy (1970, p. 827) describe electro-osmotic flow with this simple qualitative equation:

$$v_{eo} = u_{eo} \frac{\partial E}{\partial x} \quad (2-17)$$

where v_{eo} = electro-osmotic flow velocity

$\partial E / \partial x$ = electrical potential gradient

u_{eo} = coefficient of electro-osmotic mobility.

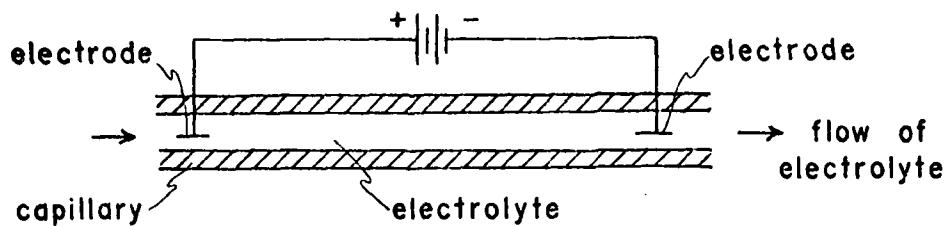


Figure 2-2. Electro-osmosis resulting from an applied potential.

Unfortunately, the literature does not quantitize the effect of electro-osmosis.

There is a companion phenomenon to electro-osmosis of interest here only for academic reasons. Not only will the presence of an electric potential produce the flow of an electrolytic fluid, but also the flow of an electrolytic fluid will produce an electrical potential. This phenomenon is called "streaming potential" and will occur when an electrolyte flows through a capillary or a membrane under a pressure gradient (Bockris and Reddy, 1970). The streaming potential is proportional to the hydraulic pressure gradient creating the flow of fluid.

Osmosis was discussed here because it may be a factor in the field application of the electrochemical technique. Osmosis was not a factor in the experimental phase of this study because the test systems were saturated and sealed so that no fluid was allowed to flow.

2-4-2-3. Diffusion Coefficient

The diffusion coefficient is an essential value for many of the calculations made in this study. Equations (2-12) and (2-14) illustrate how the diffusion coefficient is used in the basic diffusion calculations. It will be shown in Chapter 4 that the frozen tube method can be used to produce reasonable values for the diffusion coefficient. For that reason diffusion coefficients will be discussed in detail. Diffusion coefficients can either be determined experimentally or calculated using theoretical equations. The primary method for determining any physical coefficient must, of course, be based on experimental work. We will look at previous experimental work which produced diffusion coefficient data, particularly for aqueous solutions of copper. Then we will look at several different methods which have been used to calculate theoretical values for diffusion coefficients. The theoretical equations will show what factors that other researchers have felt determined the value of the diffusion coefficient.

Harned and Owen (1958) compiled data on the diffusion coefficients for many aqueous electrolytes, as derived from extensive experimental work performed by Harned and others in the late 1940's and early 1950's. It was not until the 1970's that experimental work was published showing consistent values for diffusion coefficients of the aqueous salts of copper. The most complete of these recent studies was published by Woolf and Hoveling (1970) who used the diaphragm cell method to study diffusion of copper sulfate solutions. More recently a capillary diffusion apparatus was used

by Luk and others (1975) and Ahn (1976) to determine diffusion coefficients for aqueous copper sulfate. The values given by Luk and others (1975, p. 95) and Ahn (1976, p. 292) agree very closely with the values presented by Woolf and Hoveling (1970, p. 2407). Tables 2-1 and 3-2 show some of these values for the diffusion coefficient of copper sulfate taken from the literature for the sake of comparison. A great deal of effort has been expended in the past in attempts to derive general equations for diffusion coefficients based on other physical characteristics of the solutions. Five of these equations will be discussed here in order to show different approaches and different levels of complexity.

The simplest equation for the diffusion coefficient may be this Arrhenius equation (Manheim, 1970, p. 307):

$$D = k_a e^{-Ea/RT} \quad (2-18)$$

where D = diffusion coefficient

k_a = activation constant

Ea = activation energy

R = gas constant

T = absolute temperature.

Manheim (1970) gives no units for this equation, he does not know how to determine values for k_a or Ea , nor does he show that he has, in fact, used this equation to calculate values for the diffusion coefficient. The main purpose of Equation (2-18) is to show a simple relationship of temperature to the diffusion coefficient.

Table 2-1. Comparison of D values for CuSO_4

Concentration (moles/liter)	Diffusion Coefficient (cm^2/sec)	References
0.0025	0.745×10^{-5}	Ahn, 1976
0.01	0.713×10^{-5}	Woolf & Hoveling, 1970
0.04	0.632×10^{-5}	Woolf & Hoveling, 1970
0.05	0.63×10^{-5}	Luk and others, 1975

A more useful approach assumes that the factor controlling diffusion is the resistance of the fluid to the movement of a particle based on the radius of the particle. Following is a series of equations based on the Plank-Einstein relation which will easily produce numerical values for diffusion coefficients (Katchalsky and Curran, 1967, p. 71).

$$D = RT\omega \quad (2-19)$$

where D = diffusion coefficient (cm^2/sec)

R = gas constant (8.315×10^7 dyne $\text{cm}/\text{deg mole}$)

T = temperature ($^{\circ}\text{K}$)

ω = molar mobility (cm mole/dyne sec).

Molar mobility, ω , is calculated as the inverse of resistance.

$$\omega = \frac{1}{N_A F} \quad (2-20)$$

where N_A = Avagadro's number ($6.023 \times 10^{23} \text{ mole}^{-1}$)

F = coefficient of friction of a spherical particle of radius r in a medium of viscosity η (dyne sec/cm).

$$F = 6\pi r\eta \quad (2-21)$$

where r = particle radius (cm)

η = viscosity (poises).

There are two obvious faults to this approach: (1) this equation assumes that the diffusion coefficient is a constant and does not take into account its variation with concentration, and (2) it does not account for any of the thermodynamic characteristics of the solute but merely differentiates between substances on the basis of particle radius.

The Nernst-Hartley equation, Equation (2-22), is an improvement over the Plank-Einstein equation because it incorporates some of the electrochemical parameters of the solution, but it is still relatively simple and easy to handle (Wendt, 1974, p. 648).

$$D = \frac{RT}{F^2 10^7} \left(\frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2} \right) \frac{(z_1 + |z_2|)}{|z_1 z_2|} \quad (2-22)$$

where D = diffusion coefficient (cm^2/sec)

R = gas constant (8.314×10^7 erg/mole deg)

T = temperature ($^{\circ}\text{K}$)

F = Faraday's constant (96,493 coulombs/e)

λ_1, λ_2 = equivalent ionic conductance of the cation and the anion respectively ($\text{ohm}^{-1} \text{cm}^2/\text{equiv}$)

z_1, z_2 = valance of the cation and the anion respectively (equiv/mole).

Equation (2-22) is a slight modification of one presented by Robinson and Stokes (1955, p. 297).

$$D^0 = \frac{RT}{F^2 10^7} \left(\frac{\lambda_1^0 \lambda_2^0}{\lambda_1^0 + \lambda_2^0} \right) \frac{(z_1 + |z_2|)}{|z_1 z_2|} \quad (2-23)$$

where D^0 = limiting diffusion coefficient of a solution at infinite dilution (cm^2/sec)

λ_1^0, λ_2^0 = limiting equivalent ionic conductance of the cation and the anion respectively ($\text{ohm}^{-1} \text{cm}^2/\text{equiv}$).

Limiting diffusion coefficient is strictly a theoretical parameter because it cannot be measured experimentally, but it is a useful term which is used in other calculations such as Equation (2-30).

The most complex equations discussed here are based on the work of Onsager and Fuoss (1932). They developed general equations for diffusion by rewriting Fick's first law equation (Onsager and Fuoss, 1932, p. 2759-2770).

$$J = - \Omega \text{ grad } \mu \quad (2-24)$$

where J = molecular flux,

μ = chemical potential,

and the coefficient of diffusion, D , is

$$D = \Omega (\partial \mu / \partial C)_{P,T} \quad (2-25)$$

In these equations C equals concentration of the solute, but Ω is an undefined variable. From these expressions Onsager and Fuoss

(1932) developed a series of complex equations in terms of physically measurable characteristics of the solute, solvent, and solution. Based on this work of Onsager and Fuoss, Harned and Owen (1958, p. 243) proposed the following equation for the diffusion coefficient of a single salt in dilute solution. Harned and Owen (1958) did not present units of measure for the following equations, and I did not provide them because these equations are included here for illustration and not calculation.

$$D = (v_1 + v_2) \cdot 1000RT \left(1 + C \frac{\partial \ln \gamma_{\pm}}{\partial C}\right) (1.074 \times 10^{-20}) \frac{\lambda_1^0 \lambda_2^0}{v_1 |Z_1| \Lambda^0} + \frac{\Delta \bar{M}'}{C} + \frac{\Delta \bar{M}''}{C} \quad (2-26)$$

where v_1, v_2 = number of cations and anions produced by the dissociation of one molecule of electrolyte

R = gas constant

T = temperature

C = concentration

γ_{\pm} = mean molar activity coefficient of the electrolyte

$|Z_1|$ = magnitude of the valence of the ion indicated

λ_1^0, λ_2^0 = limiting equivalent ionic conductance

Λ^0 = limiting equivalent conductance of the electrolyte

$\Delta \bar{M}', \Delta \bar{M}''$ = electrophoretic terms defined below.

$$\Delta \bar{M}' = - \frac{(|z_2| \lambda_1^0 - |z_1| \lambda_2^0)^2}{(\lambda^0)^2 |z_1 z_2| (v_1 + v_2)} \frac{3.132 \times 10^{-19}}{\eta^0 (\epsilon T)^{1/2}} \frac{C \sqrt{\Gamma}}{(1+Ka)} \quad (2-27)$$

$$\Delta \bar{M}'' = \frac{z_2^2 \lambda_1^0 + z_1^2 \lambda_2^0}{(\lambda^0)^2} \frac{9.304 \times 10^{-13}}{\eta^0 (\epsilon T)^{1/2}} C^2 \theta(Ka) \quad (2-28)$$

where η^0 = viscosity of solvent

ϵ = dielectric constant of solvent

Γ = ionic concentration ($\Gamma = \sum C z^2$) (not to be confused with ionic strength)

κ = reciprocal of average ionic radius

a = activity of solute

$\theta(Ka)$ = function defined by the following equation.

$$\theta(Ka) = e^{2Ka} (Ei(2Ka)) / (1 + \kappa a)^2 \quad (2-29)$$

where $Ei()$ = exponential integral function.

These equations, complex as they are, provide diffusion coefficients only for solutions below 0.05 normality. For more concentrated solutions the difference between calculated and observed values of D appears to be a function of concentration. Onsager and Fuoss (1932) felt that these discrepancies are the result of two effects, viscosity and hydration of the ions, which are not taken into account in their equations.

Another approach to the concept of diffusion was taken by Hartley and Crank (1949) who created the artificial term of "intrinsic diffusion coefficient." The intrinsic diffusion

coefficient is itself a theoretical concept which is not directly measurable; it is defined in terms of the rate of transfer of a substance across a section fixed so that no mass transfer occurs. Wishaw and Stokes (1954, p. 2068) called upon this idea in their work to produce yet another general equation for the diffusion coefficient of 1:1 electrolytes.

$$D = \left(1 + \frac{d\ln\gamma_{\pm}}{dC}\right) (1 - 0.018hC) \left[1 + 0.018C\left(\frac{2D^*_{H_2O}}{D^0} - h\right)\right] \left[\alpha(D^0 + \Delta_1 + \Delta_2) + 2(1 - \alpha)D_{12}\right] \frac{\eta^0}{\eta} \quad (2-30)$$

where C = concentration (moles/liter)

γ_{\pm} = mean molar ionic activity coefficient (dimensionless)

h = hydration number (dimensionless)

$D^*_{H_2O}$ = self-diffusion coefficient of water (2.43×10^{-5} cm²/sec)

D^0 = limiting diffusion coefficient of the solute (cm²/sec), Equation (2-23)

α = degree of ionic dissociation (dimensionless)

η^0 = viscosity of water (poise)

η = viscosity of solution (poise)

$\Delta_1 = \bar{\Delta M}_1$ } the electrophoretic terms as defined by
 $\Delta_2 = \bar{\Delta M}_2$ } Harned and Owen (1958); given in this paper
as Equations (2-27) and (2-28).

D_{12} = diffusion coefficient of an isolated ion pair (cm²/sec), calculated by Equation (2-31)

$$D_{12} = BTu_{12} \quad (2-31)$$

where B = Boltzmann's constant (1.38×10^{-16} erg/deg)

T = temperature ($^{\circ}$ K)

u_{12} = absolute mobility of the ion pair (cm sec^{-1} /dyne).

This equation includes the effect of both viscosity and hydration, terms not accounted for by Onsager and Fuoss (1932). The real requirement for any equation is that it must produce values which correspond closely with experimentally observed values. Wishaw and Stokes (1954) have shown that Equation (2-30) is remarkably successful.

Woolf and Hoveling (1970) used the equation of Wishaw and Stokes (1954), Equation (2-30), to calculate values for the diffusion coefficient of copper sulfate for comparison with their experimentally derived values, and they showed remarkable correlation between calculated and observed values. Because of this, and the fact that Woolf and Hoveling's (1970) data is supported by other published experimental data (Luk and others, 1975; Ahn, 1976), the present study will use their values for diffusion calculations and comparison with experimental results.

2-4-2-4. Distribution of Ionic Species and Complexing

The chemical distribution of dissolved species and complexing are topics which must be discussed together even though they may have slightly different connotations. The distribution of ionic species means the relative distribution of a dissolved metal among

its different oxidation states depending upon the geochemical conditions of the solution. However, the distribution of ionic species also includes the complexing of the dissolved metal with other substances that may be present in the water. It is important in this study to examine both the relative proportions and actual concentrations of ionic species in order to guide and understand the experimental results. This discussion includes a general review of the parameters which control the distribution of dissolved species and a specific discussion of the complexing of copper with dissolved organic substances.

The theoretical approach to studying the distribution of ionic species in electrochemical systems was most fully developed over many years by Pourbaix, culminating in his Electrochemical Atlas (1966) and by Garrels and Christ (1965). They developed the now well-known Eh-pH diagram. The basic premise is that any chemical reaction involving oxidation or reduction can be expressed at equilibrium as a function of pH and electrode potential. The equation which expresses an equilibrium reaction can then be represented as a line on an Eh-pH diagram. By writing all of the possible reactions which take place in a particular aqueous system, the Eh-pH diagram can be partitioned into fields representing the areas of dominance of various species in the system. Figure 2-3 shows the equilibrium distribution of some of the aqueous copper species. Solid chemical substances are confined to distinct areas on such a diagram, outlined by arbitrary contours of the activity of the dissolved species.

There are many reasons for understanding the distribution of ionic species in our system. It is desirable to know the pH range over which the free metal ion is dominant, such as cupric ion in the copper system. The free metal ion is the only ion which is immediately reducible to native metal at the cathode, and it may also be an ion which we wish to remove from the porous medium. In any system containing dissolved metal, there will exist a family of ions. The positive ions will be influenced to migrate toward the cathode by the electric field. Ionic migration toward the cathode aids in the removal process. Neutral ionic species, on the other hand, are not affected by the electric field. In some cases oxides and hydroxides can be formed at the cathode instead of pure metal (Pourbaix, 1966). In other cases, at very low pH, hydrogen will be generated at the cathode instead of the reduction of ions to metal; this type of competing reaction will decrease current efficiency and removal of the contaminant.

A further complication which may be encountered in a natural system is complexing of copper and other metals with dissolved organic species. Since a great deal of work has been done in this area, some generalizations can be stated. Khan (1969) studied the interaction between the humic acid fraction in soils and certain selected metal cations. He found that cupric ion complexed with humic acid more readily than manganese, cobalt, nickel, and zinc divalent ions, but less readily than aluminum and iron trivalent ions, assuming similar conditions for each case. Rashid (1971)

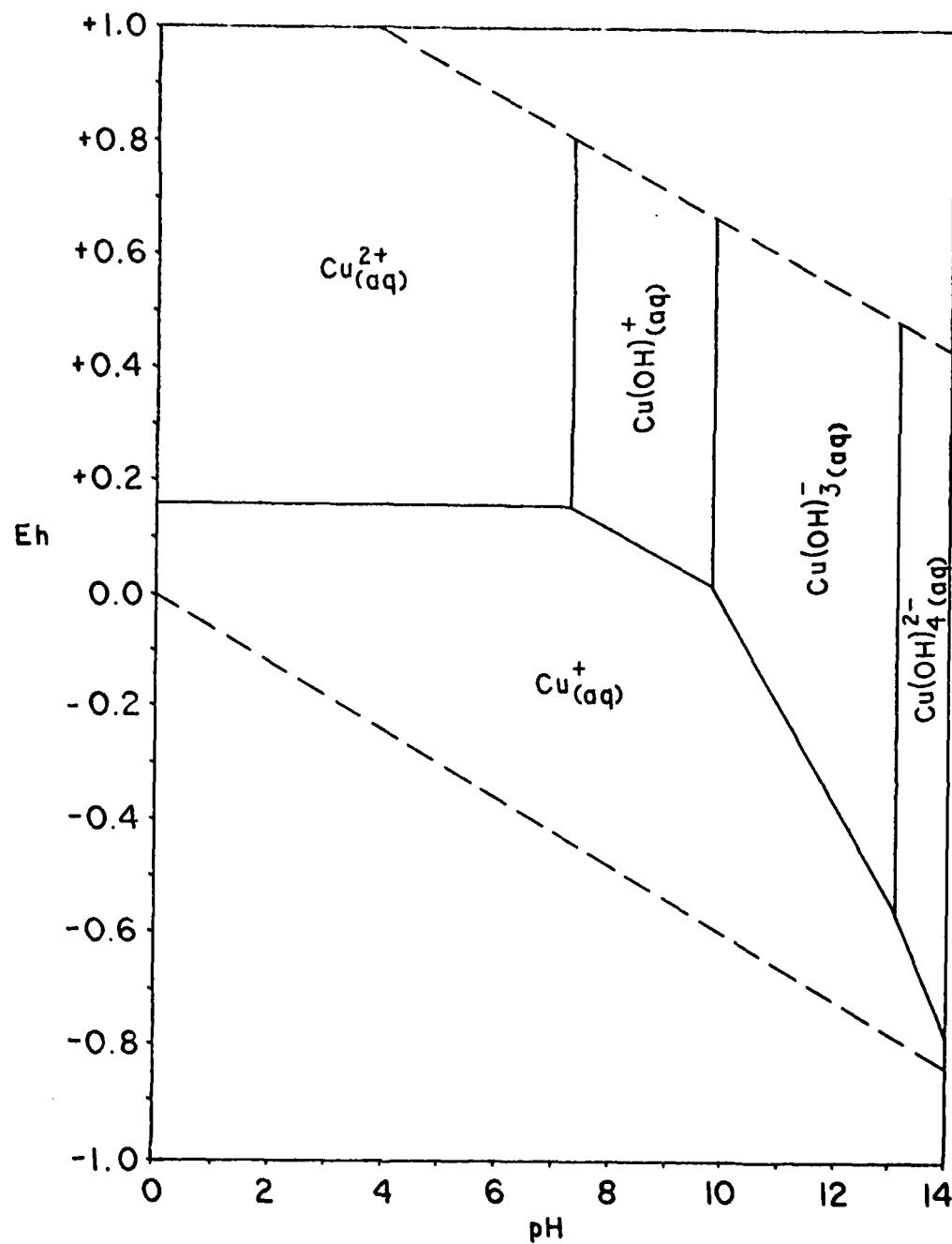


Figure 2-3. Equilibrium distribution among some aqueous copper species in the $\text{Cu}-\text{H}_2\text{O}-\text{O}_2$ system at 25°C and 1 atmosphere total pressure. (Based upon data from Naumov and others, 1971).

found that the molecular weight of the organic matter affected complexing; the lower molecular weight fraction complexed up to six times more metal than the higher molecular weight fraction. Schnitzer and Hansen (1970) studied metal-organic complexing in the fulvic acid system. They concluded that pH and fulvic acid concentration affected the complexing ratio of acid to metal, and that copper complexed readily with fulvic acid between pH 3 and 5. Rosen and Williams (1978) worked specifically on organo-cupric ion complexes and found that the relative stability of the available ligands, as well as pH, controlled the equilibrium condition.

While some authors (Kahn, 1969) feel that a variety of types of reactions are involved in metal-organic complexing, Cheam (1973) feels that the reaction is an ion-exchange type in which the metal ion displaces the hydrogen ions of the organic acid and forms a chelate. This reaction mechanism would account for the dependence of complexing on pH that other authors have reported. Chelation is also supported by Rashid's (1971) conclusion that metals reacting with organic matter appear to have lost their ionic characteristics.

Out of the summary given above, two facts are clearly meaningful to this study: first, metal-organic complexes are pH dependent and, secondly, such complexes may display nonionic characteristics. In a field situation, if metal-organic complexes are present, the mobility of a neutral complex will not be affected directly by the application of an electric potential. However, a change in pH between the electrodes which accompanies the reduction at the cathode may release some of the cupric ions from complexation for migration and removal. Although we must be aware of the possible role of

copper-organic complexes in nature, they will not be considered quantitatively in this study.

2-4-2-5. Dissolved Oxygen

An obvious question which may come to the mind of a reader of this report is, "What would the effect of the presence of dissolved oxygen in a solution be upon the effort to remove dissolved metal from that solution electrochemically?" In looking at possible analogies to the proposed electrochemical technique, the answers may appear contradictory. In polarography the presence of dissolved oxygen often interferes with determination of metallic species so oxygen removal is ordinarily the first step in polarographic analysis (Skoog and West, 1971). On the other hand, the industrial process for the electroplating of copper does not include the removal of dissolved oxygen from the plating bath. For this process the plating vats are open to the air and the plating solution is agitated; in fact, in some plants the agitation of the plating bath is accomplished by bubbling air through the solution (Ollard and Smith, 1964).

We can look for an answer to the question in thermodynamics using the following expression of the Nernst equation (Huheey, 1972, p. 156):

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{\prod \text{ products}}{\prod \text{ reactants}} \quad (2-32)$$

where E = the electromotive force of the reaction (volts)

E° = the standard electrode potential of the reaction
(volts)

R = gas constant (1.987 cal/deg mole)

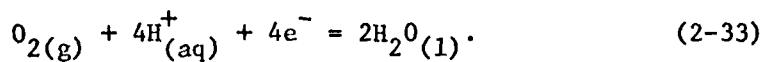
T = temperature ($^{\circ}$ K)

n = number of electrons transferred in the reaction
(equiv/mole)

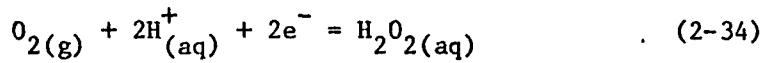
F = Faraday's constant (23,062.3 cal/volt equiv)

Π = product of ionic activities raised to the power of
their stoichiometric coefficients.

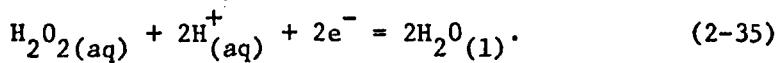
Using the international convention on signs, the reaction will proceed spontaneously when E is a positive value. There are two competing electrochemical reactions, the reduction of dissolved oxygen and the reduction of dissolved copper, and the Nernst equation can be used to determine which reaction will proceed and under what conditions. The overall reaction for the cathodic reduction of oxygen is (Hoare, 1968, p. 124):



However, this reaction occurs in two major steps:



and



The first major step, Equation (2-34), is driven electrochemically by the electrodes, but the second major step, Equation (2-35), proceeds spontaneously in the presence of a catalyst. The platinum of the electrodes used in the experimental work of this study will act as a catalyst (Hoare, 1968). The iron and manganese found in many geological materials, such as soils, will also catalyze the reaction in Equation (2-35) (Sato and Mooney, 1960). Therefore, the reaction in Equation (2-34) appears to be the one which will compete with the reduction of dissolved metal. The cathodic reduction of dissolved copper can be expressed by this reaction (Raub and Müller, 1967, p. 45):



In order to use the Nernst equation, Equation (2-32), to compare the reactions, Equations (2-34) and (2-36), it is necessary to know the pH, the activity of dissolved oxygen, the activities of hydrogen peroxide and dissolved copper, and the standard, unit activity, electrode potential relative to hydrogen for these reactions. The values of pH = 4.5 and dissolved copper activity of 0.01 moles/liter were used because they correspond with the experimental conditions used in this study. According to Breck (1974), the concentration of dissolved oxygen in oxic waters varies between 0 and 5×10^{-3} moles/liter. The worst case value of 5×10^{-3} moles/liter was used for calculation. No attempt was made to determine the activity coefficient of dissolved oxygen in this

system because it would only decrease the value of oxygen activity used for calculation, and the largest possible value is adequate as a general indicator of how the reaction will proceed. Sato (1960) estimated that the activity of hydrogen peroxide in surface waters may be poised at 10^{-6} times the oxygen activity. For Equation (2-34), $E^{\circ} = + 0.6824$ volt and for Equation (2-36), $E^{\circ} = + 0.337$ volt (Huheey, 1972, p. 260, 261).

Using the Nernst equation, we find that both reactions, Equations (2-34) and (2-36), should take place spontaneously at the cathode, but that the EMF of the oxygen reduction is a larger positive value than that of the copper reduction. This does not mean that the dissolved oxygen must all be reduced before the reduction of dissolved copper can begin. Based on the concentrations of each material, both reactions can proceed simultaneously. A portion of the electrical current would go to each reaction which would reduce the current efficiency of reducing dissolved copper.

The Nernst equation indicates that the reduction of dissolved oxygen gas should theoretically occur in the industrial electroplating process. The activity of dissolved copper would have to be greater than $10^{8.67}$ moles/liter before the EMF of the copper reaction, Equation (2-36), would thermodynamically exceed the EMF of the oxygen reaction, Equation (2-34). Current efficiency will be discussed later, but it should be sufficient to say here that, if the reduction of dissolved oxygen does occur in commercial electroplating, it does not have a serious negative effect (Smith and others, 1979).

These theoretical calculations might be used as general indicators of which reaction will occur. However, problems exist in that the mechanism of oxygen reduction is very complex, and some of the values used for calculation are estimates. For example, Breck (1974) feels that Sato's (1960) estimate of hydrogen peroxide activity is too high.

A comparison of the mechanisms of chemical transport utilized in polarography with those utilized by the proposed electrochemical technique may be useful. Polarography is based on the proposition that diffusion controls the transport of dissolved materials to the dropping mercury cathode (Skoog and West, 1971). In the proposed electrochemical technique, two mechanisms of transport, diffusion and ionic mobility, should supply dissolved metal cations to the cathode for reduction. Dissolved copper exists as a positively charged ion in acid solutions which will migrate toward the cathode in the presence of an electrical field, whereas dissolved oxygen is a neutrally charged molecule which will not be affected by an electrical field. Therefore, in the experimental system tested in this study, the total flux of dissolved copper migrating toward the cathode may be significantly greater than the total flux of dissolved oxygen.

Experimental data can be weighed against these considerations. No effort was made to remove dissolved oxygen from the test solutions used in the frozen tube experiments. It will be shown in Chapter 4 that in a simulated groundwater containing 60 ppm

dissolved copper, the level of dissolved copper was easily reduced to 15 ppm in the area of the cathode. In this experiment the reduction of dissolved oxygen may also have occurred, but if it did, it did not adversely affect the removal of dissolved copper at these concentrations.

Another experimental observation was made specifically as a test for the possible effect of dissolved oxygen on the rate of reduction of dissolved copper. Two bright platinum electrodes were immersed in a solution of copper sulfate of 0.01 molar concentration contained in a beaker open to the air. The solution of copper sulfate was not stirred or, in any way, agitated. An electrical potential of 2.50 volts was induced across the platinum electrodes, and within three minutes the distinctive color of metallic copper appeared on the cathode. The reduction of dissolved copper appeared to be instantaneous, and the rate of reduction of dissolved copper was not observably retarded by whatever dissolved oxygen may have been present in the solution. For comparison, a similar experiment was run in which the dissolved oxygen was removed by bubbling nitrogen gas through the solution. The observable results were the same; the color of metallic copper appeared on the cathode within three minutes.

In summary, the electrochemical reduction of dissolved oxygen in oxic waters is thermodynamically possible. However, the proportion of electrical current expended on the reduction of dissolved oxygen relative to that spent on reduction of dissolved copper in the proposed electrochemical technique is probably not significant.

This conclusion is supported by experimental data. It is suggested here that this may be so because the dissolved oxygen molecule is neutrally charged and will be transported to the cathode by the mechanism of diffusion, whereas dissolved copper is present as a positively charged ion which will be transported to the cathode by two mechanisms, diffusion and ionic mobility.

2-4-3. Interaction with Substrate

The set of geochemical conditions which are imposed by the porous medium, such as ion exchange and reactivity, could seriously affect the utilization of the electrochemical technique for cleanup of some field sites. This would depend on the nature of the porous medium which may be inert or non-inert. An inert porous medium would impose no geochemical conditions and would, therefore, be easier with which to work. A pure quartz sand could probably be considered as an inert porous medium. Such a sand was used as the porous matrix in the laboratory phase of this study to preclude some of the possible complications which will be discussed here. A non-inert porous medium is, unfortunately, probably a more realistic model of a natural environment. Such a medium may itself react chemically with the liquid which saturates it, or it may be responsible for adsorption or ion exchange.

2-4-3-1 Chemical Reaction

A chemically reactive substrate is virtually impossible to deal with in general terms; each such medium would have to be dealt

with as a unique and special case and will not be further considered in this study. Chapter 5 discusses the possibility of using the frozen tube method to investigate specific cases of this nature.

2-4-3-2. Adsorption and Ion Exchange

Adsorption and ion exchange will be discussed here in qualitative terms. This discussion will review the mechanisms of adsorption and ion exchange, the materials which display these mechanisms, and some of the previous attempts to model them. Although adsorption and ion exchange were not investigated in the present laboratory work, they may be factors which must be considered in the field application of the electrochemical technique. This section will also show why the frozen tube method should be a valuable tool for predicting the results of using the electrochemical technique to clean up a specific field site.

Adsorption and ion exchange are both extremely complex phenomena, but they must be discussed together. There are several adsorption mechanisms, but most of them are based on an electrostatic bonding of the metal ion to the surface of the particle. The adsorbed ion can subsequently be replaced by another ion by the process of ion exchange. The forces which hold adsorbed ions to particles range from weak to very strong and depend upon the chemistry of the solution as well as the nature of the ion and the nature of the substrate (Krauskopf, 1979). Van Olphen (1977) describes the adsorption mechanism in terms of the electric double layer around the particle. The double layer consists of the charge

on the particle and a surrounding layer of oppositely charged ions held in aqueous suspension a finite distance from the particle. The charge on the particle itself can result either from: (1) imperfections in the crystal structure of the particle which result in a net charge on the particle or (2) the preferential coating of the particle by a material with a charge (Jenne, 1968). Both mechanisms are observed in nature.

Metal ions can be adsorbed directly on the surface of clay particles (Grim, 1968). Much empirical as well as theoretical work is being done on this subject (Koppelman and Dillard, 1977; Frost and Griffin, 1977; Sidle and Kardos, 1977). Wentink and Etzel (1972) showed that copper could be removed from solution by ion exchange with loam, silt loam, and silty clay loam, and that exchange capacity increased as the clay mineral content increased. Fetter (1978) pointed out that the work of Wentink and Etzel (1972) was conducted with solutions of ions of a single metal in distilled water. Any natural system would likely also carry quantities of sodium, calcium, magnesium, potassium, and other ions which would compete for ion exchange sites in the soil. O'Connor and Kester (1975) studied the adsorption of copper on illite as a function of pH, and Farrah and Pickering (1976a,b) studied the adsorption of copper on kaolinite, illite, and montmorillonite as a function of pH. Both investigators showed that copper adsorption dropped off drastically in all cases below pH 5. O'Connor and Kester (1975) interpreted their results to mean that at lower values

of pH metal ions are removed in exchange for surface-bound hydrogen ions. Farrah and Pickering (1976b) concluded, however, that pH controls the development of hydroxyl bridges which link the metal ions to the surface of the clays. Yet another hypothesis was offered by Kopelman and Dillard (1977) who proposed that copper is adsorbed onto clays as $\text{Cu}(\text{OH})^+$. Although the specific mechanisms of adsorption are not particularly important to this study, the generalities are important because of their possible effect on the proposed technique of environmental cleanup.

Another set of materials in nature responsible for adsorption of metal ions are the oxides and hydrous oxides of iron, manganese, and aluminum. These oxides are nearly ubiquitous in clays, soils, and sediments, both as partial coatings on other minerals and as discrete oxide particles, but their common occurrence as coatings allows the oxides to exert chemical activity far out of proportion to their total concentrations (Jenne, 1968). Three factors appear to dominate the adsorption capacity of the hydrous oxides of iron, manganese, and aluminum: (1) aging, (2) pH, and (3) impurities. The crystalline nature of the oxides appears to be a function of age. Fresh hydrous oxides of iron and aluminum are amorphous, but aging of their solutions produces geothite (Landa and Gast, 1973) and gibbsite (Hsu, 1966), respectively. This transformation from amorphous material to a more crystalline state affects the surface properties of the oxides and greatly reduces their adsorption capacity (Shuman, 1977). Parks (1965) quantitatively described the

effect of both pH and impurities on adsorption capacity by the "isoelectric points" of these oxides. He uses the terms isoelectric point (IEP) and zero point of charge (ZPC) synonymously to mean the pH at which the charge on the colloidal particles is neutralized by the solution. Van Olphen (1977) differentiates between these two terms. He states that the above definition is correct for zero point of charge, and that isoelectric point is the point at which the electrophoretic mobility of the particles is zero but the surface charge is not necessarily zero.

The foundation of much of the quantitative work being done today on adsorption is the mathematical expression originally developed by Langmuir (1918) to describe the adsorption of a gas on the surface of a pure solid. The equation, now called the Langmuir isotherm, is also used in its original form to describe the adsorption of various ions in sediments and soils. The equation, as repeated by McCallister and Logan (1978, p. 88), is

$$C/(X/M) = C/b + 1/k_e b \quad (2-37)$$

where C = final solution concentration ($\mu\text{g}/\text{ml}$)

X/M = quantity of ion adsorbed per unit mass of adsorbent ($\mu\text{g}/\text{g}$)

b = adsorption maximum ($\mu\text{g}/\text{g}$)

k_e = a parameter related to the energy of adsorption ($\text{ml}/\mu\text{g}$).

If the observed adsorption conforms to the Langmuir isotherm, a plot of C versus $C/(X/M)$ will be linear, and values for k_e and b can be found from the slope and intercept of the curve. The paper by McCallister and Logan (1978) is representative of many of the current empirical studies on adsorption; it defines adsorption of a specific metal on a specific substrate in a specific environment.

Even when the adsorption datum from a specific environment conforms to the Langmuir isotherm, it cannot be used to build a general model. As Olsen and Watanabe (1957) point out, agreement of adsorption data with the Langmuir equation "does not necessarily imply any specific adsorption or reaction mechanism." Veith and Sposito (1977) also discovered that the Langmuir equation may describe empirical data obtained from a precipitation reaction. This situation is chemically meaningless to adsorption and only tends to confuse the primary purpose of the Langmuir isotherm as a description of adsorption.

Several modern attempts have been made to derive mathematical expressions for ion exchange and adsorption. Ion exchange models are fairly simple, and calculations can be based completely on values derived from experimental data (James and others, 1975). On the other hand, adsorption models are generally based on theoretical values. The model developed by Yates and others (1974) is used to calculate the theoretical density of surface charge of the ions. Although this model is qualitatively very good, it suffers from some quantitative deviation from experimental observations. The

model developed by James and Healy (1972) describes the competition between the changes in free energy which are favorable and those which are unfavorable to adsorption. James and others (1975) pointed out that the James-Healy model requires one critical assumption to be a good predictive tool, and that is the selection of a free energy value for adsorption. This value cannot be measured directly because of the amorphous state of the adsorbents.

These modern attempts to model adsorption do not solve the problem of modeling in the field environment. They are primarily confined to highly restricted laboratory systems. Krauskopf (1979) states that "despite the importance of adsorption and ion exchange, our knowledge regarding them is still largely empirical. So many variables are involved, and some are so difficult to control, that experiments all too often lead only to broad generalizations rather than to specific rules." Ellis (1973) further points out that no single equation, empirical or otherwise, has been successfully applied to the widely varying conditions of the natural environment.

It is the complexities of adsorption and ion exchange and the inability of researchers to adequately model these phenomena that increase the value of the frozen tube method as an empirical tool for studying these mechanisms. The frozen tube method offers potential both for predicting the results of using the electro-chemical technique on a specific site and for studying the mechanisms of adsorption and ion exchange in general terms.

2-4-4. Electrochemical Parameters

The last set of geochemical conditions to be discussed are those which are externally imposed on the system by the introduction of electrodes. This section is important to the present study because the parameters discussed here are those which are directly responsible for the achievement of the goal of metal removal. The topics that will be examined are the electrical parameters imposed by the electrodes, the condition of the electrode surfaces, the reactions which take place at the electrode-electrolyte interface, the electrochemical mobility of the ions, and the conductance of the electrolytic solution.

The electrical parameters imposed by the electrodes that will be examined here are the same parameters as those which are of interest to the electroplating industry. Even though the goal in electroplating is similar to the goal of this study, the electrical parameters will be different because of different operating environments. These electrical parameters are voltage and current density.

2-4-4-1. Voltage

Voltage, or electrode potential, is a parameter which must be controlled by the power source. Maximum voltage is limited by the possibility of hydrogen evolution at the cathode (Lyons, 1974). The voltage should be set at the highest value allowed without evolution of hydrogen gas because once such evolution begins, reduction of the dissolved metal contaminant will cease. For

reduction of dissolved copper this value varies depending upon the composition of the solution and the electrodes, but, in general, the value will be between one and four volts (Ollard and Smith, 1964). In industrial electroplating, the composition of the plating solution is maintained fairly constant, so the electrode potential may also remain constant. In a natural or field situation, as envisioned in this discussion, the composition of the solution will vary by design, and the electrical potential may have to be varied with time to prevent the evolution of hydrogen gas.

2-4-4-2. Current Density

Current density is also a parameter which is very important to the electroplating and electrorefining industries. Current density is a measure of the electrical current flowing per-unit of surface area of the cathode which is immersed in an electrolytic solution (Raub and Müller, 1967). Current density is measured in terms of amperes per square foot by the industrial community. In electroplating, an optimum current density has usually been experimentally determined for each system. A great deal of effort has been expended to increase current densities in the industrial processes because the rate of metal deposition is a direct function of the current density (Smith and others, 1979). In contrast, in the electrochemical technique proposed in this report, current density can be measured but not easily controlled.

The relationship between current and voltage is defined by Ohm's law (Fitzgerald and Higginbotham, 1957, p. 5).

$$I = E/R_e \quad (2-38)$$

where I = current (amperes)

E = voltage (volts)

R_e = resistance (ohms)

Voltage is a parameter which is restricted by the stability of water as already discussed, and resistance is controlled by the composition of the solution. Although resistance will change with time, it probably cannot be externally controlled in the field application of the electrochemical technique. This means that current also is a quantity fixed by the system.

Whereas current density is related to the rate of metal deposition, total current is related to total deposition. Although we cannot control current density in the system on which the electrochemical cleanup technique may be used, we can influence the total amount of current which will flow by controlling the total surface area of the cathode which will be immersed. Therefore, in the field utilization of the electrochemical technique, a cathode with the largest surface area which is practical should be used.

2-4-4-3. Electrode Surfaces

The physical condition of the electrode surfaces will affect the electrochemical removal of dissolved metal from solution. The surface must be clean and free of any contaminant which would restrict the flow of electrons or reduce the adhesion of reduced metal. In the industrial process, electrodes are cleaned in organic solvents (Oillard and Smith, 1964). An industrial procedure is

probably adequate for field use, but laboratory work requires a different method. Since platinum electrodes are used in the laboratory, the method of scouring the surface of the electrodes with a paste of powdered pyrex glass in glycerine is one method that is recommended (Doyle, 1968).

2-4-4-4. Ionic Mobility

Whenever charged ions in solution are subjected to an electrical field, the random movement of the ions is replaced by a nonrandom drift of each ion toward an oppositely charged electrode. This is known as ionic mobility. Bockris and Reddy (1970, p. 370) define conventional ionic mobility as the velocity of drift of an ion, resulting from the force of the electrical field:

$$u_i = (v_d)_i / (\partial E / \partial x) \quad (2-39)$$

where u_i = ionic mobility of ion i ($\text{cm sec}^{-1}/\text{volt cm}^{-1}$)

$(v_d)_i$ = drift velocity of ion i (cm/sec)

$\partial E / \partial x$ = force of the electrical field (volt/cm).

The ionic mobility of an ion in solution can be calculated by a very simple relationship (Robinson and Stokes, 1955, p. 42):

$$u_i = \frac{\lambda_i}{F} \quad (2-40)$$

where u_i = ionic mobility of ion i ($\text{cm sec}^{-1}/\text{volt cm}^{-1}$)

λ_i = equivalent ionic conductance of ion i ($\text{ohm}^{-1} \text{cm}^2 \text{ equiv}^{-1}$)

F = Faraday's constant (96,493 coulombs/equiv).

The ionic mobility of ions under the influence of an electrical potential results in a flux of ions toward the electrodes: cations migrate toward the cathode and anions migrate toward the anode. Bockris and Reddy (1970) called this ionic flux, the conduction flux:

$$(J_c)_i = u_i C_i \frac{\partial E}{\partial x} \quad (2-13)$$

where $(J_c)_i$ = conduction flux of ions i (moles/cm² sec)

u_i = ionic mobility of ion i (cm sec⁻¹/volt cm⁻¹)

C_i = concentration of ion i (moles/cm³)

$\partial E / \partial x$ = electrical potential gradient (volts/cm).

When a conduction flux of ions is migrating through a solution filling the pore spaces of a porous medium, the conduction flux equation is subject to the same modification as the diffusion flux equation.

$$(J_c)_i^* = \Phi T (J_c)_i \quad (2-41)$$

where $(J_c)_i^*$ = conduction flux of ions i per unit area of porous medium (moles/cm² sec)

Φ = porosity (dimensionless)

T = tortuosity (dimensionless)

The phenomenon of ionic mobility should aid in removal of metal ions from solution by contributing to the flux of positively charged metal ions toward the cathode where they can be reduced to their native state.

2-4-4-5. Reactions at Electrode Surfaces

When an ion comes into intimate contact with an electrode, an electrochemical reaction may occur. The reactions which take place at the electrode-electrolyte interface fall into three categories: (1) electron transfer with reduction, (2) electron transfer with oxidation, and (3) electron transfer without either reduction or oxidation. The transfer of electrons without either reduction or oxidation is better known as electrolytic conductance.

2-4-4-5-1. Reduction at the Cathode

Reduction takes place at the cathode with a transfer of electrons from the electrode to the ions. Although the reduction of dissolved oxygen gas at the cathode was already discussed, the best-known reaction at the cathode is the reduction of dissolved metal ions to their native metallic state. This is the reaction which the proposed electrochemical technique hopes to utilize to actually remove a dissolved metal contaminant from a saturated porous medium.

The mechanism of reduction can be discussed from a theoretical standpoint. Bauer (1972) suggested that the reduction of a metal ion at a cathode could be viewed as a step-wise process which includes the dehydration of the aquo-metal complex. He also pointed out, however, that the existing models for the process of charge transfer are largely hypothetical and speculative.

Electrodeposition may be very complex in multicomponent systems. Two or more metals may be deposited simultaneously. In industry this is done by controlling the concentrations of the various ions so that the individual potentials for deposition of the desired ions stay the same or very close (Faust, 1974). In a natural environment the concentration of a dissolved metal may be maintained at some steady-state level if the solution is in contact with a solid mineral containing that metal, or if the solution is moving, a continual fresh supply of metal ions is provided. However, even if one of these conditions exists, it seems improbable that the potentials for deposition of two or more metals would be set at the same values. The electrodeposition of two or more metals may occur simultaneously in a natural environment, but if it would, it would more likely occur as a step in the depositional sequence.

2-4-4-5-1-1. Current Efficiency

Faraday theorized that in an aqueous system with a single dissolved metal, every electron transferred from the cathode contributes to the reduction of the dissolved metal. Thus, from Faraday's law a theoretical weight of metal deposited on the cathode can be calculated from the quantity of electricity which passes through the system. Faraday's law can be expressed by the following equation (Raub and Müller, 1967, p. 26):

$$W_{\text{theory}} = \frac{Q_e W_{\text{ge}}}{F} \quad (2-42)$$

where W_{theory} = theoretical weight of metal deposited (grams)

Q_e = quantity of electricity (coulombs)

W_{ge} = weight of metal per equivalent (grams/equiv)

F = Faraday's constant (96,493 coulombs/equiv).

Since Faraday's law does not work in general practice exactly as Faraday proposed and current can also pass through the system by mechanisms other than reduction, the actual weight of metal deposited on the cathode is observed to always be less than W_{theory} . The ratio of actual weight of metal deposited to theoretical weight is called "current efficiency" (Raub and Müller, 1967). Current efficiency is a very important term in any electrochemical system because it relates to the cost of removal of dissolved metal from solution. Current efficiency in the industrial electroplating process of copper is commonly around 85%, but values as high as 99% are possible (Smith and others, 1979). Current efficiency will be reported for all experiments performed in this study.

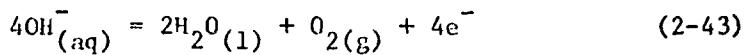
2-4-4-5-2. Oxidation at the Anode

Electron transfer with oxidation is the complimentary reaction which must take place at the anode whenever the electron transfer with reduction occurs at the cathode. This is an electrochemical reaction involving the transfer of electrons from ions in solution to the anode. A variety of oxidation reactions are possible. The three that will be discussed here are the dissolution of the anode, the evolution of oxygen gas, and the oxidation of anions.

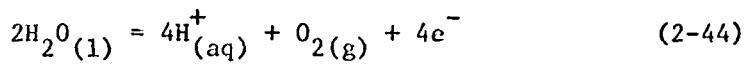
A common oxidation reaction is the dissolution or corrosion of the anode. In electroplating, the anode is made of the same metal as is being plated onto the cathode. This aids in maintaining the concentration of the dissolved metal in the plating bath at a constant level. In fact, additives are added to the plating bath to promote corrosion of the anode (Lyons, 1974). However, in a system where removal of dissolved metal is the goal of the process, corrosion of the anode poses a problem. The anode would have to consist of a metal which, if dissolved and dispersed in the porous medium, would not be considered a detrimental contaminant. Platinum is usually used for laboratory experiments because it permits operating at high overvoltages, and it does not participate in any obvious reaction at either electrode. However, platinum is too expensive for use in a field application of the electrochemical technique for pollution control, and some other substance must be substituted. In most field situations perhaps iron or aluminum would suffice.

Some electrodes are considered inert since they do not dissolve with the passage of current. The platinum electrodes used in laboratory experiments are such electrodes. They will, however, promote another type of oxidation, such as the evolution of oxygen gas. Oxygen evolution can take place at insoluble anodes by two processes (Raub and Müller; 1967, p. 42):

in alkaline solutions

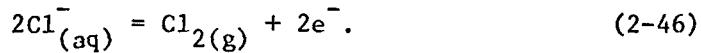
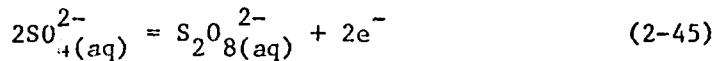


in acid solutions

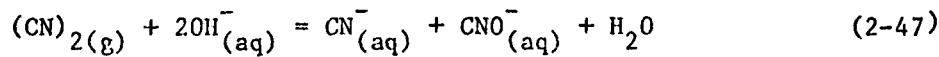


The pH of the solution is decreased by either reaction.

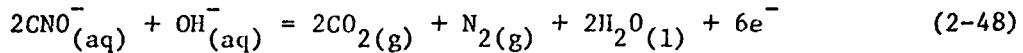
Anions can also be oxidized at the anode; Raub and Müller (1967, p. 42) give the following examples:



In some circumstances the oxidation of anions could have positive environmental results. The oxidation of cyanide ions may be such a reaction. Kuhn (1972) reviewed the processes by which cyanide ions are oxidized. Cyanide can ultimately be decomposed to carbon dioxide and nitrogen gases at the anode. The problem with this process lies in the fact that the first step in the sequence is the formation of cyanogen gas, $(\text{CN})_2$, at the anode. Cyanogen gas is highly toxic and flammable, but it is water soluble (Cotton and Wilkinson, 1972). Cyanogen gas hydrolyzes by the following reaction in both acid and basic solutions but rapidly only in base (Cotton and Wilkinson, 1972, p. 298).



The CNO^- ion then is oxidized at the anode by the following reaction (Kuhn, 1972, p. 305).



It should be noted that it is possible for several of these anode reactions to occur simultaneously.

2-4-4-5-3. Conductance

Conductance is the ability of an electrolytic solution to transmit an electrical current. The symbol for conductance of a solution is Λ and it is expressed in units of cm^2/ohm equivalent (Bockris and Reddy, 1970). From the units it can be seen that conductance is the inverse of resistance. In fact, conductance is physically measured in terms of resistance. In a binary solution the conductance of the solution is said to be the sum of the conductance of each ion (Glasstone, 1942, p. 80):

$$\Lambda = \lambda_+ + \lambda_- \quad (2-49)$$

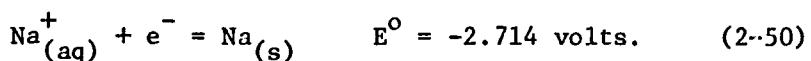
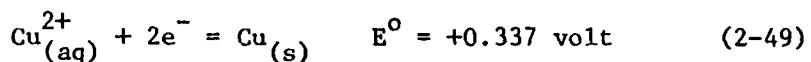
where Λ = equivalent conductance of the solution (cm^2/ohm equiv)

λ_+ = equivalent ionic conductance of the cation (cm^2/ohm equiv)

λ_- = equivalent ionic conductance of the anion (cm^2/ohm equiv).

In aqueous solutions some dissolved metal ions are reduced to their native state at the cathode while others are not. For example, dissolved copper can easily be plated onto a cathode from a

solution of copper sulfate, but dissolved sodium will not be reduced to the metallic state at a cathode from an aqueous solution. The differences between these occurrences can be explained thermodynamically by the Nernst equation, Equation (2-32). The reactions of interest are listed below and their standard electrode potential were taken from published tables (Huheey, 1972, p. 257, 260):



By using these values in the Nernst equation it is found that cupric ion should be spontaneously reduced (positive EMF) at the cathode at 25°C in all cases where the cupric ion activity is greater than $10^{-11.4}$. Therefore, copper can theoretically be removed from solution by electrodeposition to the point where its concentration is insignificant. Sodium, on the other hand, cannot be reduced to its native state at 25°C at any activity level below $10^{+46.0}$ in an aqueous solution. Because such an activity level is impossible, sodium cannot be reduced at a cathode in an aqueous solution. Sodium is, therefore, one of the ions commonly found in natural waters which is available for the conductance of electrical current.

2-4-4-5-3-1. Transference Numbers

Conductance is important to this study because it can be viewed as a competing mechanism to the removal of ions from solution by reduction. The competition can be expressed mathematically by transference number or transport number. The transference number of an ion expresses the proportion or total electrical current carried through an electrolytic solution by that species of ion. Glasstone (1942, p. 107-108) shows several equations for transference numbers starting with this equation:

$$t_i = (q_e)_i / Q_e \quad (2-51)$$

where t_i = transference number of ion i (dimensionless)

$(q_e)_i$ = quantity of electricity transmitted by ion i
(coulombs)

Q_e = quantity of electricity transmitted by all ions
(coulombs).

In a binary solution transference numbers can be expressed in terms of ionic mobility:

$$t_+ = \frac{u_+}{u_+ + u_-} \quad (2-52)$$

where t_+ = transference number of the cation (dimensionless)

u_+, u_- = ionic mobility of the cation and the anion
respectively ($\text{cm sec}^{-1}/\text{volt cm}^{-1}$).

Transference numbers may also be calculated from equivalent ionic conductance values for binary solutions:

$$t_+ = \lambda_+ / \Lambda. \quad (2-53)$$

where λ_+ = equivalent ionic conductance of the cation
 $(\text{ohm}^{-1} \text{ cm equiv}^{-1})$

Λ = equivalent conductance of the solution
 $(\text{ohm}^{-1} \text{ cm equiv}^{-1})$.

Bockris and Reddy (1970, p. 401) show that for a multicomponent system the transference number is also a function of ionic concentration and charge:

$$t_i = \frac{z_i C_i u_i}{\sum z_i C_i u_i} \quad (2-54)$$

where z_i = valence of ion i (equiv/mole)

C_i = concentration of ion i (mole/cm³)

u_i = ionic mobility of ion i (cm sec⁻¹/volt cm⁻¹).

Transference numbers pertain only to the portion of the ionic flux produced by an electrical field. Diffusion flux, which is produced by a gradient in chemical potential, is not counted in the transference number (Bockris and Reddy, 1970). A transference number which approaches zero indicates that the ion in question will not be transported as a result of the electrical field in that particular solution. More importantly, transference numbers provide another method to calculate the conduction flux in addition to Equation (2-13). Bockris and Reddy (1970, p. 405) give the following equation:

$$(J_c)_i = \frac{t_i i_T}{z_i F} \quad (2-55)$$

where $(J_c)_i$ = conduction flux of ion i (moles/cm² sec)

t_i = transference number of ion i (dimensionless)

i_T = total conduction current per unit of cross-sectional area (amps/cm²)

z_i = valence of ion i (equiv/mole)

F = Faraday's constant (96,493 coulombs/equiv).

2-5. Summary

This chapter has attempted a complete survey of the factors which affect and control the movement and removal of metal ions from a saturated porous medium using electrochemistry. Some of these factors do not apply to the specific environments created in the experimental systems, and these factors will not be discussed further. Such factors were discussed here because of their possible effects on the field application of the proposed electrochemical technique of pollution control. Other factors which directly affect the experiments performed for this study will be discussed in more detail later. The following chapters unify the applicable factors experimentally.

The parameter of greatest interest is the quantity of metal removed per unit time. Given the composition of the solution and the physical variables of the porous medium, it would be desirable to calculate the quantity of metal removed from the system in a given amount of time with a given expenditure of electricity.

This cannot be done theoretically, but the following sections will show that it can be accomplished experimentally using the frozen tube technique of this study.

CHAPTER 3

RELATIONSHIP BETWEEN Eh AND EMF

3-1. Introduction

The purpose of this chapter is to give the reader a feeling for the relationship between passive Eh and induced EMF as they are used in this study. The electrochemical parameter used most frequently in geochemical literature is Eh. Chapter 2 contained a discussion of the meaning and usage of Eh. The Eh of a solution is commonly measured as the potential difference relative to the standard hydrogen electrode between a bright platinum electrode and a reference electrode of convenience. This study, however, centers around the effects resulting from inducing an electrical potential across a solution with electrodes. In order to show the relationship between these two parameters, a series of simple experiments were performed in the laboratory, and the results of the experiments are reported here.

3-2. Eh and EMF Experiments

The experiments reported in this chapter consisted of two basic types, the measurement of the passive Eh in solution and the measurement of the induced EMF at each electrode relative to a reference electrode. Passive Eh of each solution tested was measured with a platinum electrode and a reference electrode connected to a Beckman meter. An electrical potential was then

induced across the test solutions with a completely separate set of platinum electrodes connected to a power supply. The electrodes connected to the power supply will be called the "working electrodes." In all cases, the passive Eh electrodes were positioned between the working electrodes as shown in Figure 3-1. The working electrodes were approximately three inches apart.

The second type of experiments measured the potential difference between each working electrode and a reference electrode. The equipment configuration for this type of experiment is shown in Figure 3-2. The reference electrode was approximately centered between the two working electrodes which were about three inches apart. In this type of experiment we are able to show the electrical potential of each electrode relative to the standard hydrogen electrode.

The solutions used for these experiments also fall into two categories. The first category of solutions is electrolytes which will conduct an electrical current through the solution without participating in an oxidation or reduction reaction at either electrode. Solutions of potassium chloride and hydrochloric acid were used. The second category of solutions is one in which the cations will be reduced at the cathode. Solutions of copper sulfate were used for these tests.

There were several factors common to all experiments reported in this chapter. Bulk solutions were used in all experiments; no porous matrix was present. All solutions were open to the air, and no efforts were made to remove whatever dissolved oxygen may have been present in these solutions. The temperature of all solutions

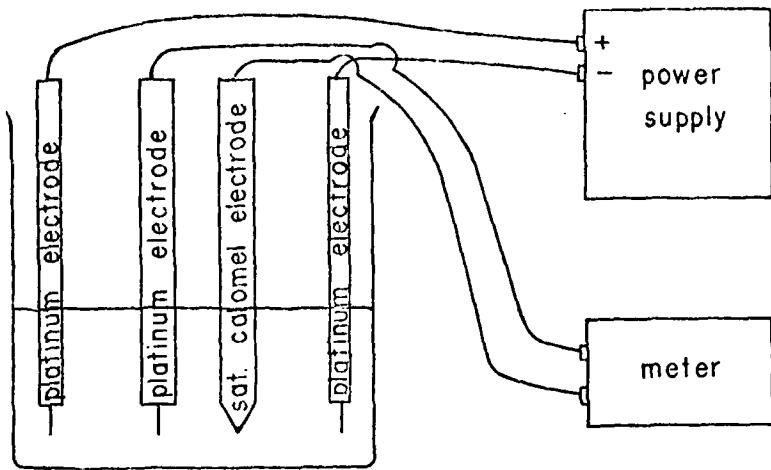


Figure 3-1. Apparatus for measuring passive Eh of a solution and inducing an electrical potential across the solution.

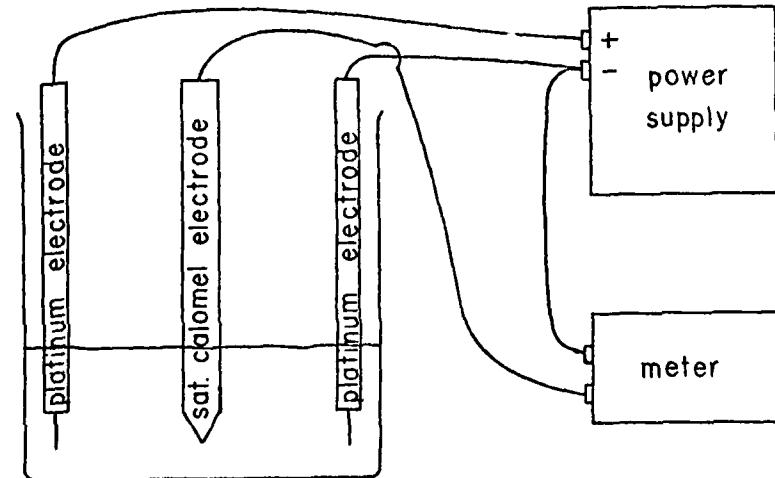


Figure 3-2. Apparatus for measuring the electrical potential between a working electrode and a reference electrode.

tested was at 25° C. Whenever the working electrodes were used, the electrical potential between them was set at a constant 2.50 volts. The reference electrode used for all of these experiments was a saturated calomel electrode. The potential of the saturated calomel electrode at 25° C is +0.2444 volt (Langmuir, 1971). Any potential measured between a platinum electrode and a calomel reference electrode can be related to Eh by the following equation (Langmuir, 1971, p. 618).

$$Eh = E(\text{observed}) + E_c \quad (3-1)$$

where Eh = electrical potential relative to the standard hydrogen electrode (volts)

$E(\text{observed})$ = electrical potential measured between a platinum electrode and a calomel reference electrode (volts)

E_c = electrical potential of the calomel reference electrode (volts).

3-2-1. KCl Solution

The first solution tested was potassium chloride in 0.01 molar concentration. Potassium chloride was chosen because it will conduct an electrical current in aqueous solution without participating in an oxidation or a reduction reaction and because of the similarities between the properties of the cation and the anion. Potassium and chloride ions have nearly equal values of limiting equivalent ionic conductance: $\lambda_{K^+}^{\circ} = 73.52 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv}$ and $\lambda_{Cl^-}^{\circ} = 76.35 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv}$ (Harned and Owen, 1958, p. 231).

Also, according to the MacInnes assumption, potassium ions and chloride ions have equal ionic activities in pure solution of potassium chloride (Garrels and Christ, 1965).

The results of these tests are shown in Table 3-1. The points discussed here are numbered for clarity in reading. (1) It should be noted that there was a slight change in the value of passive Eh when an induced current was passed through the solution with a separate pair of electrodes, but the change was only barely measurable. (2) The observed EMF between the cathode-reference pair and the anode-reference pair can be added to produce the potential between the cathode and the anode. This value of 2.51 volts is the same as the value measured with a Simpson digital multimeter. The full significance of this data will be realized when they are compared with the data from the other test solutions.

3-2-2. HCl Solution

The second test solution was hydrochloric acid in 0.01 normal concentration. Hydrochloric acid was chosen because it will also conduct an electrical current in aqueous solution without participating in an oxidation or a reduction reaction, but its individual ionic properties are dissimilar in contrast to potassium chloride. The limiting equivalent ionic conductance values for hydrogen ion and chloride ion are greatly different:

$$\lambda_{H^+}^0 = 349.8 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv} \text{ and } \lambda_{Cl^-}^0 = 76.35 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv}$$

(Harned and Owen, 1958, p. 231).

The results of these tests are shown in Table 3-2. Again, the discussion points are numbered. (1) Even though no redox

Table 3-1. Eh and EMF Data for 0.01 M KCl

passive E(observed)	= +0.230v	passive Eh	= +0.474v
passive E(observed) with 2.50v induced potential	= +0.233v	passive Eh with 2.50v induced potential	= +0.477v
observed EMF between cathode and reference	= -1.004v	EMF between cathode and reference relative to SHE	= -0.760v
observed EMF between anode and reference	= <u>+1.508v</u>	EMF between anode and reference relative to SHE	= <u>+1.752v</u>
potential between cathode and anode	= 2.512v	potential between cathode and anode	= 2.512v

SHE - standard hydrogen electrode

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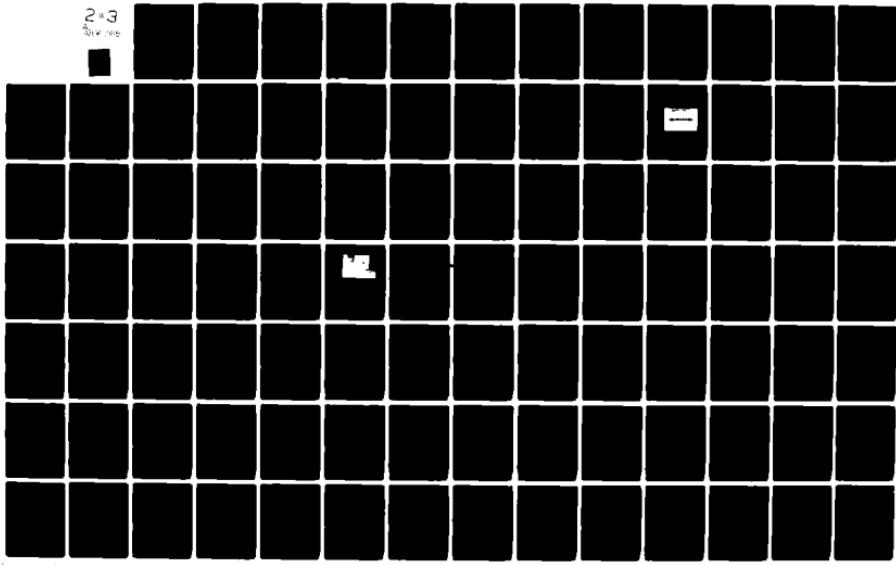


Table 3-2. Eh and EMF Data for 0.01 N HCl

passive E(observed)	= +0.310v	passive Eh	= +0.554v
passive E(observed) with 2.50v induced potential	= +0.320v	passive Eh with 2.50v induced potential	= +0.564v
observed EMF between cathode and reference	= -0.625v	EMF between cathode and reference relative to SHE	= -0.381v
observed EMF between anode and reference	= <u>+1.875v</u>	EMF between anode and reference relative to SHE	= <u>+2.119v</u>
potential between cathode and anode	= 2.500v	potential between cathode and anode	= 2.500v

SHE - standard hydrogen electrode

couple exists in the solutions of either hydrochloric acid or potassium chloride, the passive Eh values in the two solutions are markedly different. (2) When 2.50 volts of potential were applied across the solution of hydrochloric acid, a change in the passive Eh was observed. This change was larger in the hydrochloric acid solution than it was in the potassium chloride solution. It should be noted that this change is reversible: when the induced potential is turned off, the passive Eh returns to its original value observed without the flow of electrical current. (3) The potential between the cathode and the anode can again be calculated by adding the observed EMF between the cathode-reference pair and the anode-reference pair. However, in the hydrochloric acid solution, the distribution of the total potential observed between the cathode-reference pair and the anode-reference pair is different than it is in the potassium chloride solution.

3-2-3. CuSO₄ Solutions

The final set of solutions tested was prepared by dissolving anhydrous copper sulfate in deionized water. Copper sulfate was chosen because the dissolved copper ions are readily reduced to the native state at a cathode and because copper sulfate was used in the frozen tube experiments described in Chapter 4. Concentrations of 0.01 molarity and 0.001 molarity were used.

The results of these tests are shown in Tables 3-3 and 3-4. Some of these results follow the same general trends as the results

from the tests on potassium chloride and hydrochloric acid solutions, but additional information was also gained from these experiments. (1) The passive Eh is a function of the concentration of the solute. (2) When 2.50 volts of potential were induced across the solutions, a change in the passive Eh values was observed. This change was larger than that observed in either the potassium chloride or the hydrochloric acid solution. (3) Table 3-3 records an interesting phenomenon; the relative direction of change in passive Eh was reversed by reversing the positions of the passive electrodes in the solution. (4) In the three electrode systems shown in Figure 3-2, the potential between the working electrodes is distributed between the cathode-reference pair and the anode-reference pair as a function of the concentration of the solute in solution. (5) A special observation was made which is not recorded in the tables of numerical data. At the same time as metallic copper was plated onto the cathode, the bubbles of gas, presumably oxygen, were formed on the anode.

3-2-3-1. Nernst Potential

A special test was performed using the copper sulfate solutions to see if a theoretical Nernst potential could be observed experimentally. A diagram of the experimental apparatus is shown in Figure 3-3. The only difference between this apparatus and that used to measure passive Eh is that the equipment in Figure 3-3 utilizes a pure copper electrode instead of a platinum electrode.

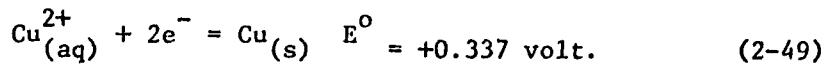
Table 3-3. Eh and EMF Data for 0.01 M CuSO_4

passive E-(observed)	= +0.310v	passive Eh	= +0.554v
passive E(observed) with 2.50v induced potential	= +0.330v	passive Eh with 2.50v induced potential	= +0.574v
passive E(observed) with 2.50v induced potential and the positions of the Pt and ref. electrodes reversed from Figure 3-1.	= +0.278v	passive Eh with 2.50v induced potential and the positions of the Pt and ref. electrodes reversed from Figure 3-1.	= +0.522v
observed EMF between cathode and reference	= -0.390v	EMF between cathode and reference relative to SHE	= -0.146
observed EMF between anode and reference	= +2.110v	EMF between anode and reference relative to SHE	= +2.354v
potential between cathode and anode	= 2.500v	potential between cathode and anode	= 2.500v
SHE - standard hydrogen electrode			

Table 3-4. Eh and EMF Data for 0.001 M CuSO_4

passive E(observed)	= +0.270v	passive Eh	= +0.514v
passive E(observed) with 2.50v induced potential	= +0.300v	passive Eh with 2.50v induced potential	= +0.544v
observed EMF between cathode and reference	= -0.770v	EMF between cathode and reference relative to SHE	= -0.526v
observed EMF between anode and reference	= <u>+1.729v</u>	EMF between anode and reference relative to SHE	= <u>+1.973v</u>
potential between cathode and anode	= 2.499v	potential between cathode and anode	= 2.499v
SHE - standard hydrogen electrode			

The copper electrode allows the metal of the electrode to actually participate in the redox reaction shown below:



In order to calculate the theoretical Nernst potential for the reduction of dissolved copper, we must use the Nernst equation. The Nernst potential is the EMF of the reaction relative to the standard hydrogen electrode as controlled by the concentration of the solute and the temperature of the solution. The Nernst equation is repeated below:

$$E = E^\circ - \frac{RT}{nF} \ln \frac{\Pi \text{ products}}{\Pi \text{ reactants}} \quad (2-32)$$

where E = EMF of the reaction relative to the standard hydrogen electrode (volts)

E° = standard electrode potential of the reaction (volts)

R = gas constant (1.987 cal/deg mole)

T = temperature ($^{\circ}\text{K}$)

n = number of electrons transferred in the reaction
(equiv/mole)

F = Faraday's constant (23,062.3 cal/volt equiv)

Π = product of ionic activities raised to the power
of their stoichiometric coefficients.

It is necessary to calculate the activity coefficients of dissolved copper in the test solutions in order to render an accurate Nernst potential. Sample calculations for the solution

of 0.01 molar concentration of copper sulfate will be shown. The activity coefficient for dissolved copper was calculated by the mean salt method starting with the following equation (Garrels and Christ, 1965, p. 60):

$$\gamma_{\pm\text{CuSO}_4} = ((\gamma_{\text{Cu}}^{2+}) (\gamma_{\text{SO}_4^{2-}}))^{1/2} \quad (3-2)$$

where $\gamma_{\pm\text{CuSO}_4}$ = mean activity coefficient of CuSO_4
(dimensionless)

γ_{Cu}^{2+} = ionic activity coefficient of Cu^{2+}
(dimensionless)

$\gamma_{\text{SO}_4^{2-}}$ = ionic activity coefficient of SO_4^{2-}
(dimensionless)

The values necessary to determine the activity coefficient of the Cu^{2+} ion and the sources are: $\gamma_{\pm\text{CuSO}_4} = 0.42$ (Garrels and Christ, 1965, p. 59, Fig. 2.14) and $\gamma_{\text{SO}_4^{2-}} = 0.47$ (Garrels and Christ, 1965, p. 63, Fig. 2.15).

$$\gamma_{\text{Cu}}^{2+} = (0.42)^2 / (0.47) = 0.38 \quad (3-3)$$

Activity and concentration are related by this equation (Garrels and Christ, 1965, p. 53):

$$a_i = \gamma_i c_i \quad (3-4)$$

where a_i = activity of ion i (moles/kg water)

γ_i = activity coefficient of ion i (dimensionless)

c_i = concentration of ion i (moles/kg water).

For these calculations we shall assume that moles/kg water are equal to moles/liter solution. All of this reduces to the following activity of Cu^{2+} ion in a solution of 0.01 molar concentration of copper sulfate:

$$a_{\text{Cu}}^{2+} = (0.38) (0.01) = 0.0038 \text{ moles/liter.} \quad (3-5)$$

The theoretical Nernst potential can now be calculated. At 25°C , Equation (2-32) can be converted to this form:

$$E = E^{\circ} - \frac{0.0592}{n} \log \frac{\prod \text{products}}{\prod \text{reactants}}. \quad (3-6)$$

The Nernst potential for reduction of Cu^{2+} ion at a pure copper electrode is calculated by inserting the proper values in Equation (3-6):

$$E = +0.337 - \frac{0.0592}{2} \log \frac{1}{0.0038} = +0.265 \text{ volts.} \quad (3-7)$$

The same procedure was followed to calculate a theoretical Nernst potential for the reduction of Cu^{2+} ion at a pure copper electrode in a solution of 0.001 molar concentration of copper sulfate.

The experimental results are compared to the theoretical values in Table 3-5. Very good correlation is shown between the theoretical Nernst potentials and the experimentally observed values. These values are grossly different from the passive Eh values measured in the same solutions using a platinum electrode (Tables 3-3 and 3-4). The final point of comparison is that the difference between the Nernst potentials for the two copper sulfate solutions

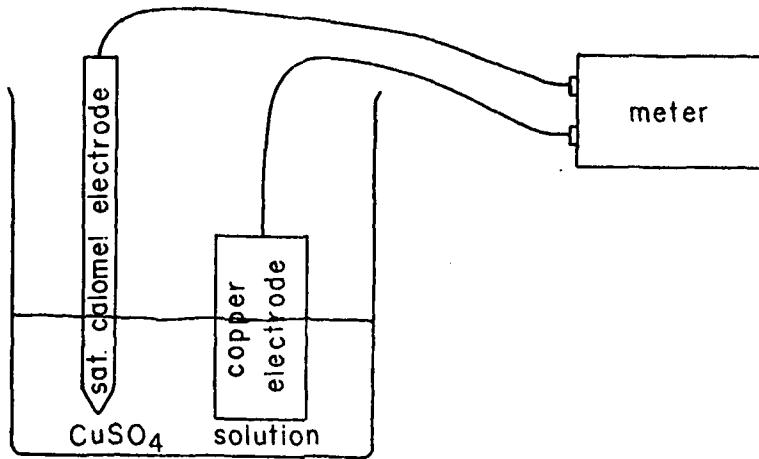


Figure 3-3. Apparatus for measuring the Nernst potential for the reduction of Cu^{2+} ion to the native state.

Table 3-5. Observed and theoretical Nernst potential data for the reduction of Cu^{2+} ion to the native state

0.01 M CuCO_4		0.001 M CuSO_4	
E(observed)	= +0.027v	E(observed)	= +0.004v
Eh based on E(observed)	= +0.271v	Eh based on E(observed)	= +0.248v
E based on theoretical calculations	= +0.265v	E based on theoretical calculations	= +0.244v

measured with the copper electrode is not the same as the difference between the passive Eh values for the same two solutions measured with the platinum electrode.

3-2-3-2. EMF Gradient

A variation of the experiment shown in Figure 3-2 was run to see if the observed potential measured between a working electrode and the reference electrode is a function of the distance between the two. A diagram of the apparatus used for this experiment is shown in Figure 3-4. The test solution for this experiment was a 0.01 molar concentration solution of copper sulfate. The reference electrode was placed at each of the seven numbered positions, and the electrical potential between the reference electrode and each numbered position.

The results of this test are shown in Table 3-6. The electrical potential between the reference electrode and the working electrode is, indeed, a function of the distance between the two electrodes. The numerical data from this test are graphically displayed on Figure 3-5. The observed EMF values appear to form a linear gradient between the working electrodes. I do not know if it is technically correct to extend the gradient lines beyond the data points. Regardless of the position of the reference electrode, the potential between the cathode and the anode can be calculated by adding the potentials between the cathode-reference pair and the anode-reference pair.

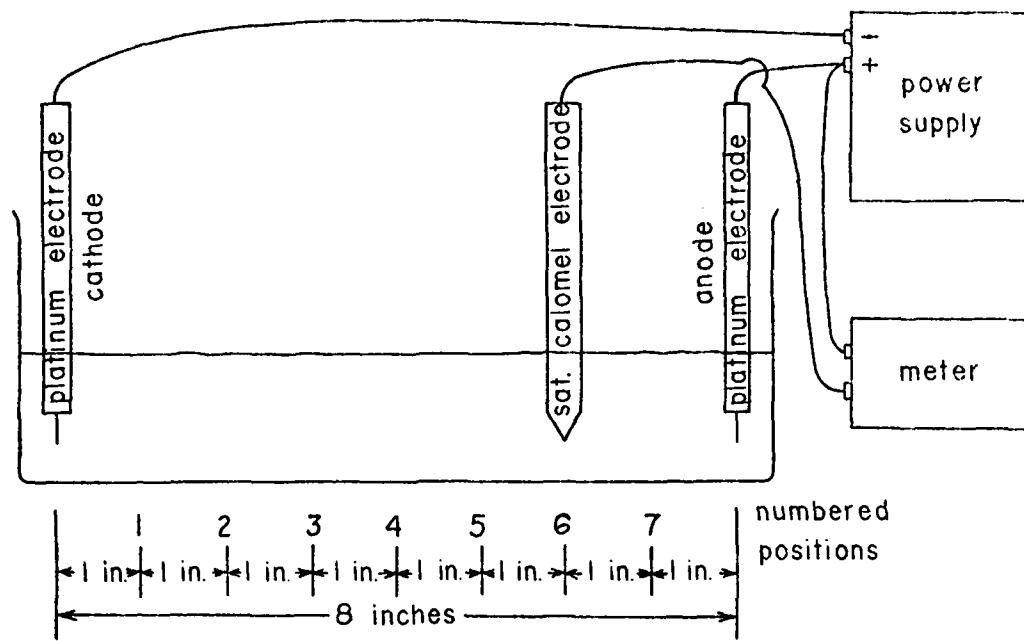


Figure 3-4. Apparatus for measuring the electrical potential between the reference electrode and a working electrode as a function of the distance between the two electrodes.

Table 3-6. EMF data for 0.01 M CuSO_4 as a function of the distance between the reference and the working electrodes

Numbered Position	Observed EMF Between Cathode and Reference	Observed EMF Between Anode and Reference	Potential Between Cathode and Anode
1	-0.235v	+2.26v	2.495v
2	-0.324v	+2.17v	2.494v
3	-0.381v	+2.11v	2.491v
4	-0.451v	+2.04v	2.491v
5	-0.508v	+1.992v	2.500v
6	-0.586v	+1.914v	2.500v
7	-0.661v	+1.840v	2.501v

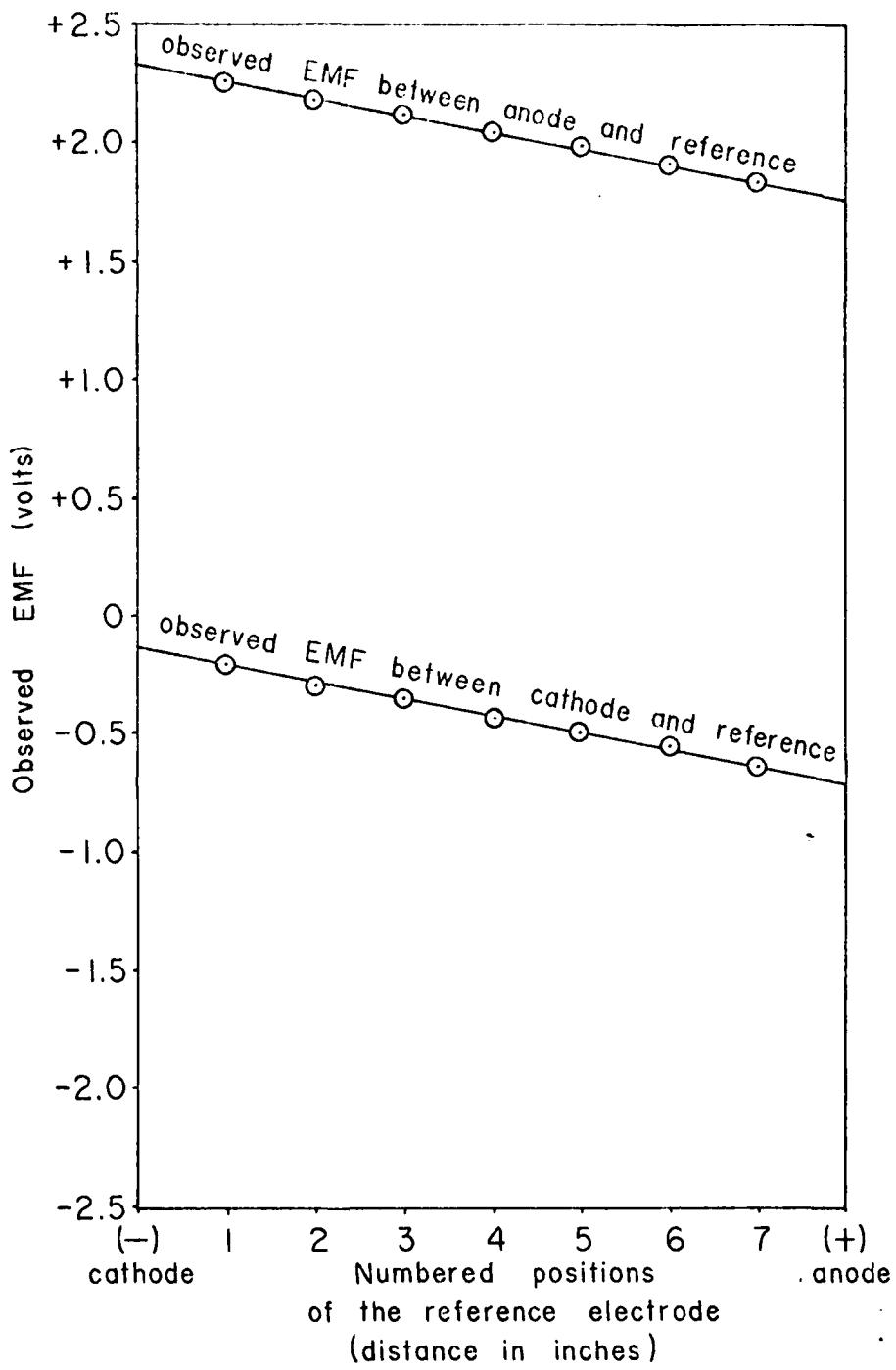


Figure 3-5. Graphical representation of EMF data for 0.01 M CuSO_4 as a function of the distance between the reference electrode and the working electrode.

3-3. Conclusions

The experimental work reported in this chapter was performed in hopes of giving the reader some insight into the relationship between passive Eh and induced EMF as they are used in this study. However, this work was not meant to satisfy any of the main objectives of this study. Therefore, the results of this work are reported without speculation about the causes of the results. The major conclusions of the experimental work reported in this chapter are summarized below.

- (1) Passive Eh may or may not be influenced by a redox reaction taking place in solution, but it is usually affected by a flow of electrical current through the solution.
- (2) The measurement of the effect of the flow of an electrical current on passive Eh is a function of the relative positions of the passive platinum and reference electrodes in that current.
- (3) The potential difference between two platinum electrodes connected to a constant-voltage power supply is an absolute value regardless of the reference used for measurement.
- (4) If a reference electrode is centered between two platinum working electrodes connected to a power supply, the difference in potential between the cathode-reference pair and the anode-reference pair is a function of the substance in solution.
- (5) If a reference electrode is centered between two platinum working electrodes connected to a power supply, the difference in potential between the cathode-reference pair and the anode-reference pair is also a function of the concentration of the solute in solution.

(6) If a reference electrode is positioned at varying locations between two platinum working electrodes connected to a power supply, the difference in potential between the reference and either platinum electrode is a function of the distance between the reference and the working electrode.

(7) The Nernst potential of a redox reaction can be measured experimentally, but it is not observed using an inert platinum electrode with a reference electrode.

CHAPTER 4

LABORATORY METHODS AND RESULTS

4-1. Introduction

The purpose of this study was to determine if the migration and removal of dissolved copper in a saturated porous medium could be controlled electrochemically with an acceptable expenditure of electricity. The laboratory technique which finally produced meaningful data is new and is called the "frozen tube method." It was developed specifically for this study.

The frozen tube method, as utilized in this study, simulates the specific field environment of a shallow groundwater. The frozen tubes contain a solution which was open to the atmosphere before it was allowed to fill the pore spaces of the porous medium. This is equivalent to an oxygen-rich surface water which percolates into a subsurface environment with a high water table.

There were several experimental conditions and parameters which were common to all tests run in this study. The first was temperature. The temperature of all experiments was controlled at 25°C by jacketing the systems with a water bath. The temperature of the water bath was maintained by a Haake constant temperature circulator accurate to $\pm 0.01^\circ\text{C}$. The second factor common to all experiments was the porous medium. An unconsolidated, medium-grained, quartz sand was selected for its quality of relative inertness. Quartz sand neither reacts nor adsorbs the dissolved species in solution.

4-2. Characterization of the Porous Medium

Three parameters of the porous medium were measured in order to define the sand used in all of the experiments reported in this chapter. The characterization of the sand by weight fraction is given in Table 4-1. The other two parameters measured were porosity and permeability.

The porosity of the sand was measured in each frozen tube as it was prepared. The simple calculation was made using this equation:

$$\Phi = V_v/V_b \quad (2-1)$$

where Φ = porosity (dimensionless)

V_v = volume of pore space (cm^3)

V_b = bulk volume of the porous medium (cm^3).

The bulk volume was the internal volume of the frozen tube, and the pore volume was the amount of solution added because the sand was completely saturated. The porosity of the sand averaged 34 percent.

The permeability of the sand was measured using a falling-head permeameter. The equation used with a falling-head permeameter renders the hydraulic conductivity of the porous medium (Todd, 1959, p. 56):

$$K_h = \frac{d_t^2 L}{d_c^2 \Delta t} \ln \frac{h_0}{h} \quad (4-1)$$

where K_h = hydraulic conductivity (cm/sec)

d_t = tube diameter (cm; 0.645 cm)

d_o = sample chamber diameter (cm; 2.76 cm)

L = sample chamber length (cm; 4.24 cm)

Δt = time of flow (sec; 10 sec)

h_o = head at $t = 0$ (cm)

h = head at Δt (cm).

The values for the permeameter used here and the time of flow are indicated above.

The sample chamber of the falling-head permeameter was filled with sand in the same manner as the frozen tubes. Three runs were made with the falling-head permeameter. The data obtained are shown in Table 4-2. A sample calculation using the data from the first run is shown below. Hydraulic conductivity is calculated by inserting the proper values in Equation (4-1):

$$k_h = \frac{(0.645)^2 (4.24)}{(2.76)^2 (10)} \ln \frac{54}{21} = 0.02187 \text{ cm/sec.} \quad (4-2)$$

Hydraulic conductivity can be converted to permeability using a conversion factor for water at 20°C (Todd, 1959, p. 328):

$$k = 1.035 \times 10^{-3} k_h \quad (4-3)$$

where k = permeability (darcys).

For the first run, the calculated value for the permeability of the sand used in this study is:

$$k = 1.035 \times 10^{-3} (0.02187) = 22.64 \text{ darcys.} \quad (4-4)$$

Table 4-1. Characterization of sand by weight fraction

Mesh Size	Grain Size (microns)	Weight Percent
>20	>840	0.02
>30, <20	>590, <840	4.96
>40, <30	>420, <590	32.62
>50, <40	>297, <420	38.88
>80, <50	>177, <297	21.42
>200, <80	>75, <177	2.09
>400, <200	>37, <75	0.01

Table 4-2. Data from the falling-head permeameter

Run	Head at $t = 0$ (cm)	Head at Δt (cm)
1	54	21
2	52	21
3	54	22

The same calculations were made for the last two runs. The average permeability of the sand used in this study is 22 darcys.

4-3. Analytical Methods

The dissolved copper species available in each experimental system were introduced by dissolving anhydrous copper sulfate. The substances of interest for which analyses were made were total copper, sulfate ion, and hydrogen ion. All analyses were performed by the researcher.

Copper concentrations were determined by the colorimetric technique using neocuproine (Diehl and Smith, 1958). Neocuproine is a specific reagent for copper. In solutions buffered with acetate, copper reacts with neocuproine to produce a soluble orange compound. The absorption of monochromatic light at a wave length of 454 m μ was measured with a Beckman DU-2 Spectrophotometer. Absorption of light is directly proportional to the concentration of copper in solution. The concentration in the unknowns was determined by comparing their absorption values with a standard curve.

A single set of standards was prepared and used for this entire study. The standards were prepared by dissolving pure copper metal in concentrated nitric acid. The concentrations of the standards were from 32.8 to 656.0 ppm copper, and the pH values of the standards were from 1.7 to 0.7 respectively. The standard solutions were stored in polyethylene bottles. Storage life for standard solutions of dissolved copper at these concentrations and pH values poses no problem to this study. Ratonetti (1976)

shows that there is no loss in copper concentration from solutions containing 0.5 to 1.0 ppm dissolved copper when the solution were below pH 3.5. Smith (1973) shows that copper solutions containing 2 to 10 ppm dissolved copper will not lose copper from solution when they are stored at pH values of or below 1.5.

A standard curve was prepared every time a set of unknowns was run. The data for the standard curve was input into a standard linear regression program in a hand calculator (Texas Instruments SR-51-II). The concentrations of the unknowns could then be determined by the calculator from the best-fit line of the standard curve and the absorption values for the unknowns. This produced statistically better data than a graphical approach.

The data from the standard curve also permitted the generation of statistical information on the accuracy of the analytical technique for determining copper concentrations in solution. The approach used was to determine the standard deviation for the standard curve for each experiment. This best represents the human error introduced in preparing and analyzing the colorimetric solutions. The slight differences between standard curves prepared on different days was not used because this represents fluctuations from one day to the next in the functioning of the spectrophotometer and in the strength of the reagents used to prepare the colorimetric solutions. These day-to-day fluctuations did not affect the data from a single experiment because the standard curve and the unknowns

were all prepared and analyzed on the same day using a single batch of reagents.

There are five steps in determining the standard deviation from standard curve data. This approach is based on the assumption that the plot of absorption versus concentration is linear. Enough plots were made of data from this study to assure that the limits of the standard curve are within the linear portion of the absorption-concentration curve. The five steps are as follows:

- (1) Input the data points for the standard curve into the linear regression program of the calculator.
- (2) Calculate the best-fit absorption value for each concentration.
- (3) Determine the deviation between the actual absorption value and the best-fit absorption value for each concentration.
- (4) Calculate standard deviation for absorption.
- (5) Translate that value into standard deviation for concentration by using the slope of the best-fit curve.

Data from twenty-four standard curves were analyzed for standard deviation, and the standard deviation values thus derived were averaged. The error introduced into results by the copper analysis technique was ± 2.0 ppm; this error represents one standard deviation. For results reported as percent of copper remaining, this error equates to $\pm 0.33\%$.

When the value of the sulfate concentration was desired, it was determined by a volumetric titration (ASTM, 1979). The

sulfate was titrated in a solution of ethyl alcohol under pH controlled conditions with a standardized barium chloride solution. Thorin was used as the indicator. ASTM (1979) states that the titration of sulfate by this method is accurate to ± 1.5 ppm.

Hydrogen ion activity was determined using a Markson pH electrode and a Beckman meter. The semi-microelectrode was used because very small quantities of the unknown were available, and the electrode did not consume any of the unknown. The activity coefficient of the hydrogen ion in each unknown was approximated using Figure 2.15, p. 63, Garrels and Christ, (1965). The ionic strength of the solutions, which was needed to use Figure 2.15 in Garrels and Christ, was calculated using the concentrations of copper and sulfate ions and the activity of hydrogen ion. Activity coefficients permitted converting hydrogen ion activities to concentration values. This method was probably the weakest analytical technique with regard to accuracy.

4-4. Frozen Tube Method

The frozen tube method is a technique which was developed by my advisor, Professor Donald Runnels, and me solely for this study. I know of no other researchers who have used this method to study ionic transport.

The general procedures of preparing the frozen tubes were standardized. In all experiments in this study the saturated porous medium was contained in cylindrical acrylic tubes with

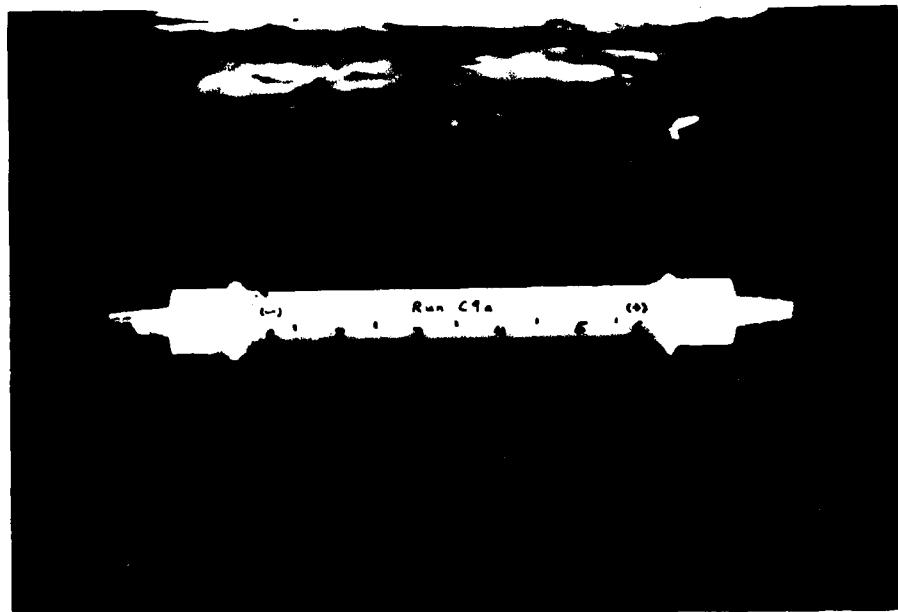


Figure 4-1. Photograph of a frozen tube ready for experimentation. This tube has platinum electrodes in either end for the application of an electrical potential.

the dimensions of 5/8 inch inside diameter, 3/4 inch outside diameter, and 6 inches long. The tubes were closed on each end with a flat plexiglas disc held in place by a plastic cap and sealed with silicone sealant. To insure that the porous medium was truly saturated, the liquid was incrementally added to the tube first; the sand was then poured into the liquid and packed with a glass stirring rod. Figure 4-1 is a photograph of a frozen tube ready for experimentation.

Each experimental run was terminated with the freezing step. The contents of the acrylic tube were frozen as rapidly as possible by immersing the tube in a Dewar flask of liquid nitrogen. The tube was allowed to be immersed for approximately five minutes. In this amount of time the vigorous boiling of the liquid nitrogen ceased which indicated that the temperature of the tube and its contents had approached the temperature of the liquid nitrogen. Since the boiling point of nitrogen is -195.8°C , the aqueous solution in the tube was not only frozen but reduced in temperature far below 0°C . This assured that all mechanisms of ionic transport were essentially halted in time and space. It also assured that the tube would stay frozen long enough for it to be sliced into sections.

While the six-inch long tube was still frozen solidly, it was sliced into six one-inch sections. The slicing was performed manually with a hack saw. Each section was then placed in a sealed beaker and allowed to thaw. After thawing the liquid contained in

each section was diluted slightly with deionized water and removed for analysis. The analyses made this way represent average concentrations within each section. It is the differences and gradients between sections that are most significant. When these sectional concentration values are plotted on a graph, the concentration gradient across the entire tube emerges.

The frozen tube method was used in the study to generate several different types of information. In one set of experiments the mechanism of diffusion was studied by itself. In three other sets of experiments the electrochemical effect of an applied potential was studied. The physical preparation of the tube varies from the general steps listed depending upon the purpose of the experiment.

4-4-1. Study of Diffusion

In the sequence of laboratory work, the study of diffusion was performed relatively late, but it will be presented first because it represents the simplest system. In the other frozen tube experiments several mechanisms of ionic transport are operating together. This experiment allowed studying a single mechanism, that of diffusion, in the same physical system in which the other frozen tube experiments were run. The work presented here offers an addition to the methods currently available for studying diffusion.

The physical preparation of a tube for a diffusion experiment was unique among the other frozen tube runs. The six-inch tube

was first cut into two pieces: one piece was one inch long and the other was five inches long. The one-inch section was filled with sand saturated with an aqueous solution of approximately 0.01 M CuSO_4 . The open end of the tube was sealed with a thin plastic membrane. The five-inch section was filled with sand saturated with deionized water. The two sections of tubing were then fitted together, and the experiment began when the plastic membrane was slipped out and removed. Figure 4-2 is a diagram of a frozen tube which was prepared for a diffusion experiment. At the end of the designated period of time, the experiment was terminated with the freezing step. The frozen tube was then cut into six one-inch sections so that the contents of each section could be analyzed.

4-4-1-1. Diffusion of Copper

This set of experiments was designed to measure and record diffusion of dissolved copper in the saturated sand. The analytical technique used here measures total copper, but at the operating conditions of Eh and pH the predominant copper species present is cupric ion (Figure 2-3).

Diffusion is a time-dependent phenomenon. This is shown graphically by the concentration-distance curves on Figure 4-3. To understand these curves one should recall how the experiment was physically constructed. At time $t = 0$, Section 1 was uniformly saturated with copper sulfate solution containing 617 ppm of copper, and Sections 2 through 6 were uniformly saturated with water (Figure 4-2). The concentration-distance curves show how the

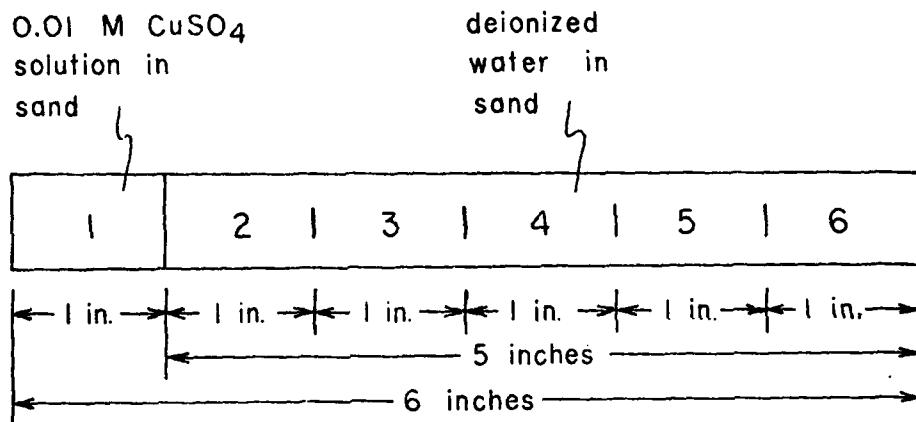


Figure 4-2. Frozen tube prepared for diffusion experiment.

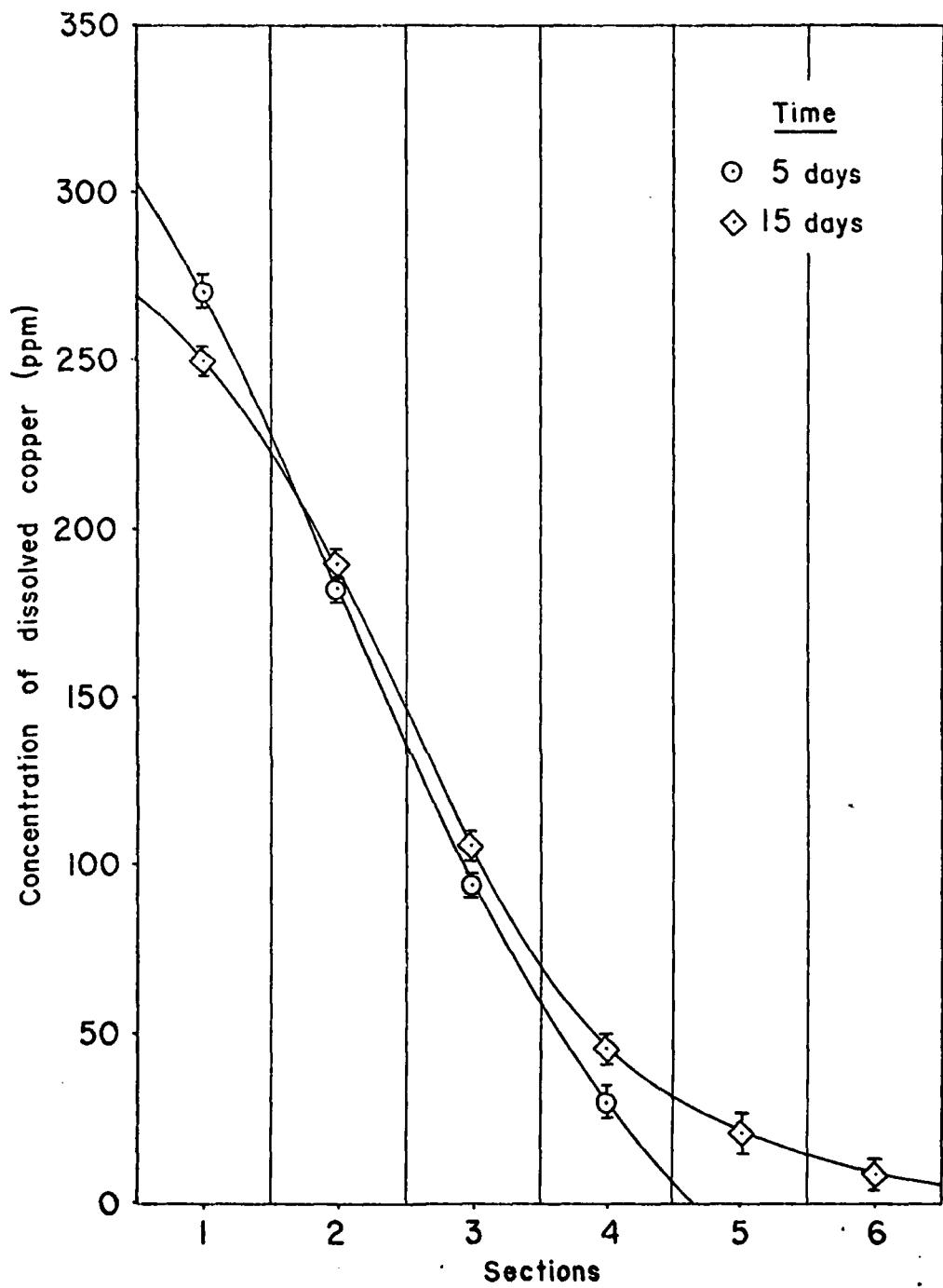


Figure 4-3. Concentration-distance curves for diffusion of dissolved copper. Two experimental runs were made for each time period; the error bars represent the value obtained for each run.

dissolved copper diffuses with time from Section 1 into Sections 2 through 6. The curve recorded after diffusion was allowed to proceed for 5 days is nearly linear, but the curve recorded after 15 days more closely assumes the standard S-shape shown by Crank (1957).

The error bars shown on the curves in Figure 4-3 reflect the fact that each experiment was run twice. The curves are drawn through the average values for each length of time. These discrepancies are the result of several factors. I believe that they are primarily the result of the fact that no two tubes can be packed with sand in exactly the same way. Discrepancies will also be introduced by mechanical and human factors in constructing and filling the plastic tubes and in performing the analyses. However, from Figure 4-3, the errors are quite small and acceptable.

Constructing and analyzing concentration-distance curves is not a new technique. Crank (1957) explains that a concentration gradient for a substance diffusing through a liquid in a glass tube can be recorded by measuring the refractive index of the liquid at numerous points at a given time. The new frozen tube method does, however, offer two improvements: (1) diffusion through an opaque geological material can be studied, and (2) all ionic transport is halted in time and space yielding detailed information on the distribution of species.

A concentration-distance curve can be used to obtain basic data about the process of diffusion. Diffusion coefficients can be calculated using Equation 4-2 (Crank, 1957, p. 233).

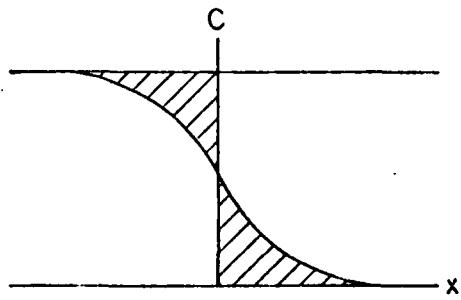


Figure 4-4. Ideal concentration-distance curve for diffusion.

$$D_{C=C_1} = - \frac{1}{2t} \frac{dx}{dC} \int_0^{C_1} x \, dC \quad (4-2)$$

where D = diffusion coefficient (cm^2/sec)

t = time (sec)

x = distance (cm)

C = concentration (Choice of units is arbitrary because they cancel out, but they must be consistent.)

The use of this equation can be better understood by looking at Figure 4-4, which is an idealized concentration-distance curve for diffusion. The position of the horizontal C -axis is chosen so that the two shaded areas are equal. A concentration is then selected arbitrarily on the lower portion of the graph as shown on Figure 4-5. The gradient dx/dC can be determined by drawing a tangent where C_1 strikes the curve. The integral $\int_0^{C_1} x \, dC$ is represented on Figure 4-5 by the shaded area. The values extracted from the

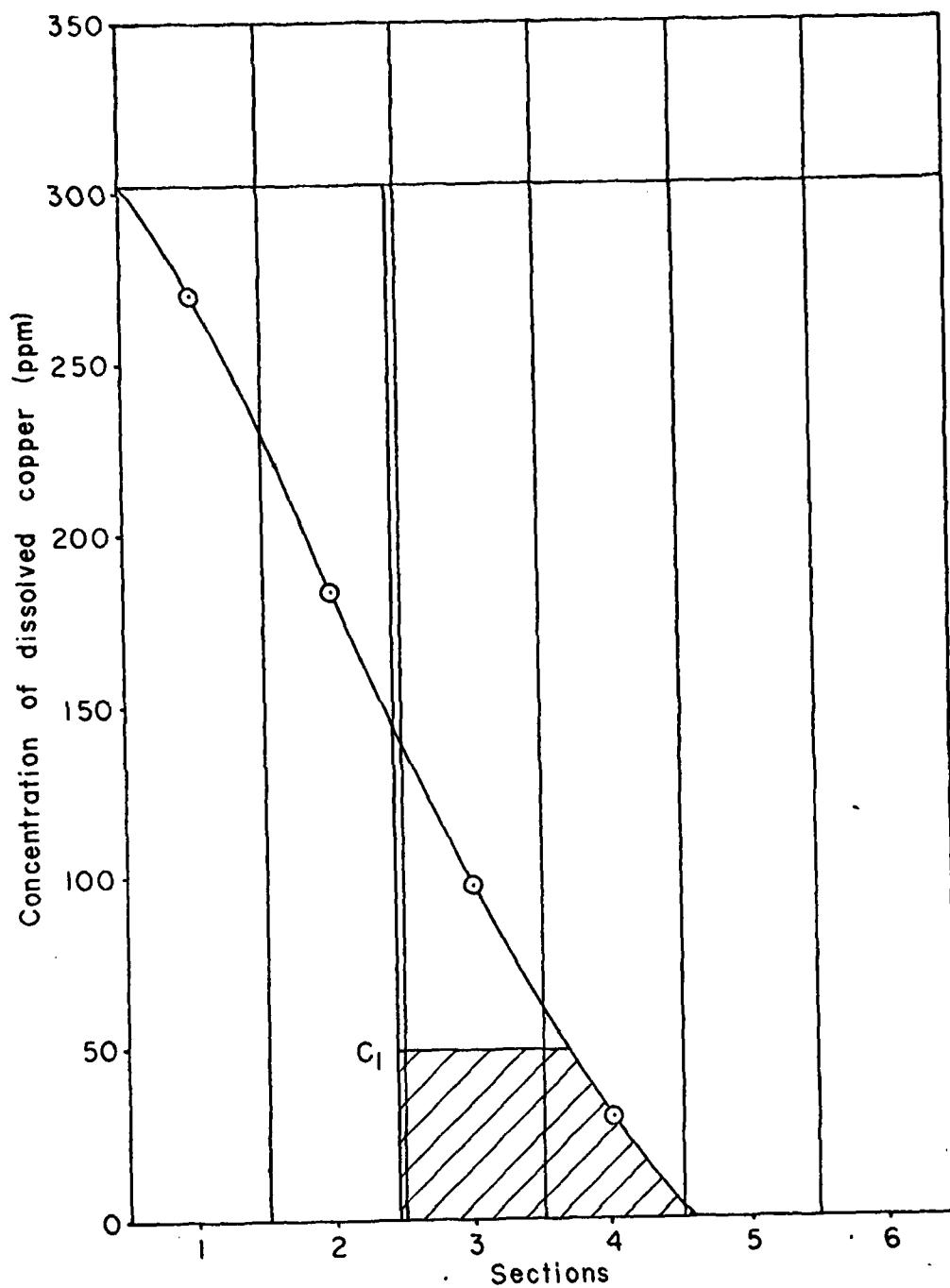


Figure 4-5. Concentration-distance curve for diffusion of dissolved copper; $t = 5$ days. The data points on this curve are the average of two experimental runs.

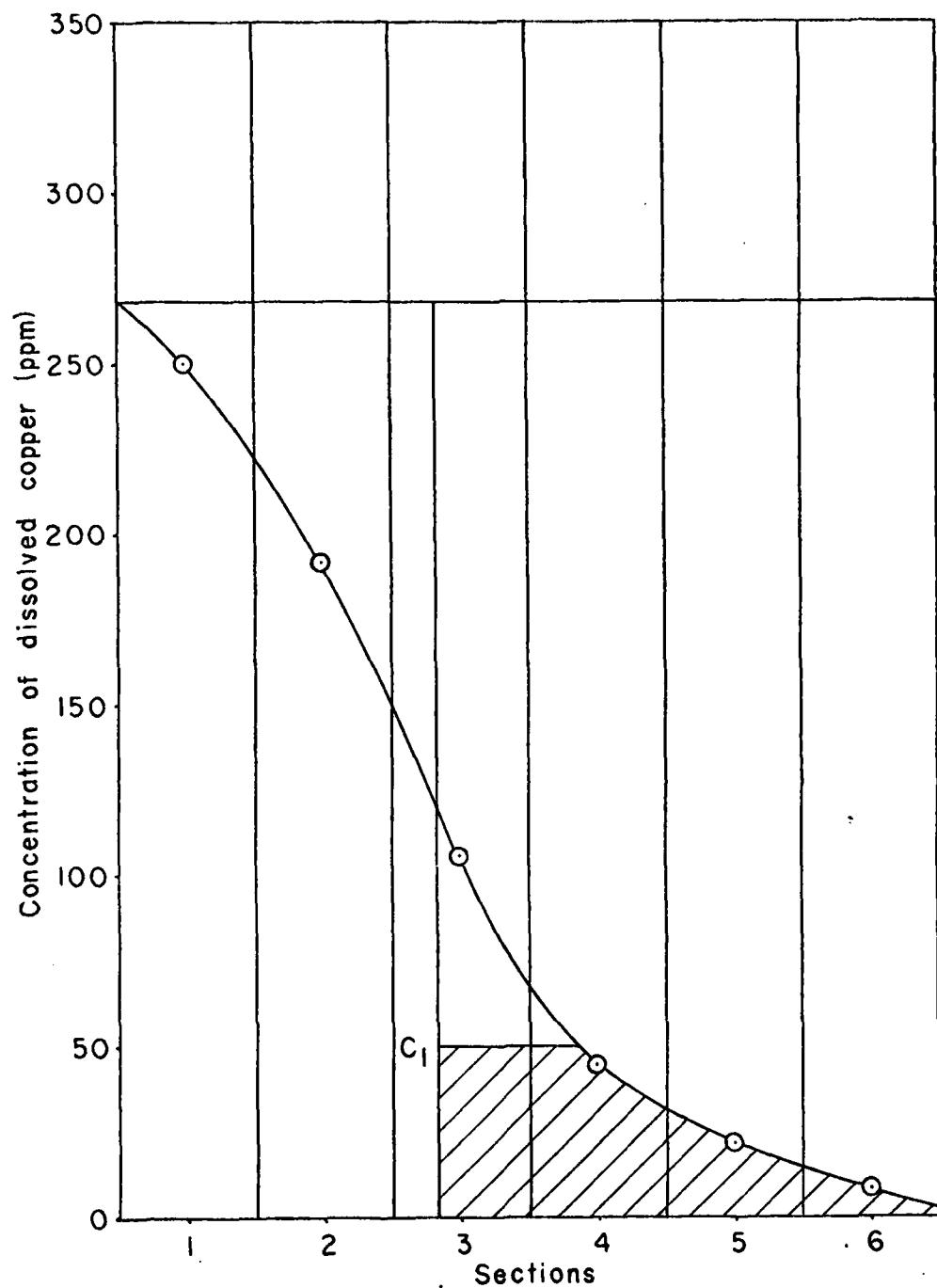


Figure 4-6. Concentration-distance curve for diffusion of dissolved copper; $t = 15$ days. The data points on this curve are the average of two experimental runs.

Table 4-3. Comparison of D values for Cu^{2+} and CuSO_4^*

Solute	Concentration (moles/liter)	$D \times 10^{-5}$ (cm^2/sec)	References
Cu^{2+}	0.79×10^{-3}	0.93 ± 0.09	Fig. 4-5, this study, $t = 5$ days
Cu^{2+}	0.79×10^{-3}	0.69 ± 0.07	Fig. 4-6, this study, $t = 15$ days
CuSO_4	0	0.858	Woolf & Hoveling, 1970
CuSO_4	0.01	0.713	Woolf & Hoveling, 1970
CuSO_4	2.50×10^{-3}	0.745	Ahn, 1976
Cu^{2+}	undefined	0.58	Eq. (2-19), this study, Katchalsky & Curran, 1967; using hydrated radius of Cu^{2+} , Nightingale, 1959

* The values published by Woolf and Hoveling (1970) are directly comparable to those determined by this study because they actually measured only the diffusion of copper. The method used by Ahn (1976) produced a mean value between the diffusion coefficients for copper and sulfate ions.

5-day curve on Figure 4-5 were used to calculate a diffusion coefficient for cupric ion. For comparison the diffusion coefficient at the same C_1 was calculated from the better developed 15-day concentration-distance curve on Figure 4-6. The results of these graphical calculations are shown in Table 4-3.

Crank (1957) states that the greatest disadvantage of using a graphical method for calculating the diffusion coefficient is the amount of error which is generated. Since the method of determining the diffusion coefficient from the data produced by this study was a graphical method, the amount of error was also determined graphically. The diffusion coefficient for dissolved copper was calculated six times each for the 5-day curve and 15-day curve. The six separate curves were the two actual curves and each of these two curves adjusted by plus 2 ppm and minus 2 ppm copper which is the value of uncertainty of the analytical technique used for copper. The standard deviation from the mean of the six values of the diffusion coefficient was then computed on a hand calculator. This method thus accounts for the errors introduced by the analytical technique, the difference in the two frozen tubes, and the human and mechanical errors inherent in the graphical determination. These errors are shown in Table 4-3 along with the diffusion coefficients.

The results of calculating diffusion coefficients by the frozen tube method are also compared to those from the literature in Table 4-3. Several general observations about these diffusion coefficients are worth noting. The diffusion coefficient of copper sulfate is not a constant but instead varies with concentration;

the diffusion coefficient decreases in value with increased concentration of the solute. The two values determined experimentally in this study are both reasonably close to those published in the literature. The value calculated from the 5-day run is, however, slightly too high. A better value was derived from the more fully developed concentration-distance curve of the 15-day run. I believe that this shows that the frozen tube method is a viable tool for studying diffusion.

There are three improvements which could be made to the procedures of this experiment to enhance the use of the frozen tube method for studying diffusion. First, the plastic tube should be placed in a vertical position with the copper sulfate solution at the bottom of the tube so that density differences in the solutions do not affect ionic transport. In this experiment the tubes were positioned horizontally. Secondly, the plastic tube should be firmly attached to a stable mount so that it is not subject to vibrations. The action of the water in the water bath in this experiment probably agitated the tube somewhat. These two factors could have contributed to slightly high values for the diffusion coefficient of cupric ion. Last, the two sections of the plastic tube should be of equal length and long enough to permit the concentration-distance curve to become asymptotic to the horizontal axis as shown in Figure 4-4.

Tortuosity plays a role in diffusion through a saturated porous medium. Using Bear's (1972) equation for tortuosity,

Equation (2-6), a value for the tortuosity of the sand in these experiments can be calculated.

$$T = D^*/D \quad (2-6)$$

where T = tortuosity (dimensionless)

D^* = diffusion coefficient in a porous medium (cm^2/sec)

D = diffusion coefficient in a bulk liquid (cm^2/sec)

The value of $0.69 \times 10^{-5} \text{ cm}^2/\text{sec}$ is used for D^* , diffusion coefficient in the porous medium. From the values cited in the literature a D value at the same concentration can be extrapolated at $0.77 \times 10^{-5} \text{ cm}^2/\text{sec}$ (Figure 4-7). The ratio of these two numbers renders a tortuosity of $T = 0.90$. To put this value for tortuosity into physically meaningful terms, Bear's (1972) equation, Equation (2-10), is used.

$$T = (L/L_e)^2 \quad (2-10)$$

where L = length of the bed of porous material in the direction of ionic transport

L_e = actual length of the path taken by the solute in traversing the bed of length L

For this unconsolidated sand the ratio L_e/L equals 1.05.

In order to use the frozen tube method for determining true diffusion coefficients (excluding tortuosity), one would have to calibrate the porous medium using a solute for which the diffusion coefficient in a bulk solution is well known as we have with copper.

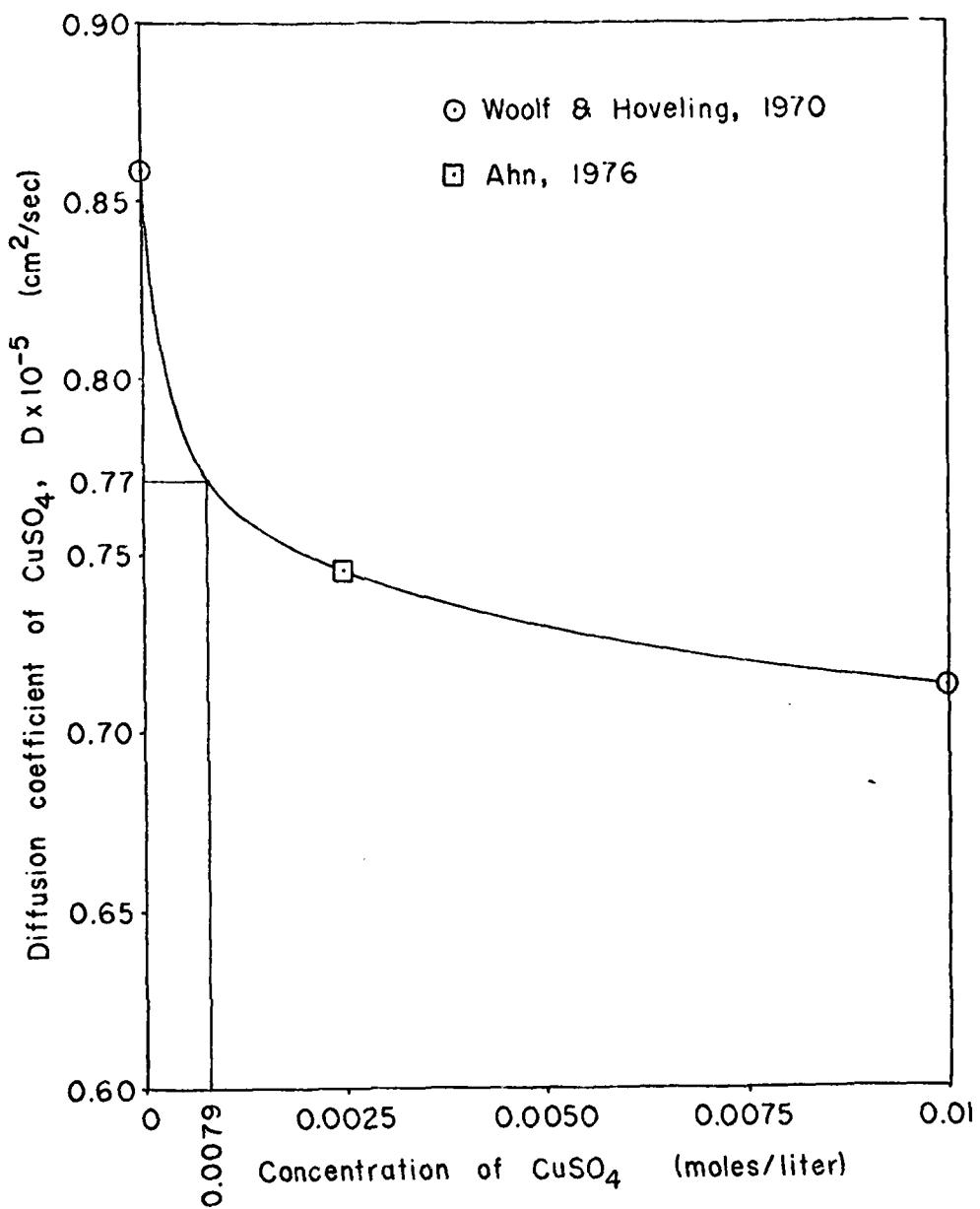


Figure 4-7. A plot of the diffusion coefficient data for copper sulfate published by Woolf and Hoveling (1970) and Ahn (1976).

This is analogous to using the diaphragm cell method (Stokes, 1951). Once the porous medium has been calibrated to determine tortuosity, the frozen tube method can be used to calculate the diffusion coefficient for any material. For applications to natural situations, determining tortuosity alone by the frozen tube method may be advantageous.

4-4-1-2. Diffusion of Sulfate

One significant advantage of using the frozen tube method to study ionic transport is that after the physical slicing of the column or tube has been accomplished, a sufficient quantity of material may be available to analyze for many individual dissolved species. An analysis for sulfate was made on one of the 5-day diffusion experiments. A minor disadvantage of performing a sulfate analysis is that some of the sample solution is consumed, thereby reducing the redundancy in the copper analyses.

The results of the sulfate analysis are shown on Figure 4-8. At time $t = 0$, Section 1 was uniformly saturated with a copper sulfate solution containing 932 ppm of sulfate ion, and Sections 2 through 6 were uniformly saturated with deionized water. The curve of Figure 4-8 represents the concentration-distance curve for sulfate ion after diffusion was allowed to proceed for 5 days.

The concentration-distance curve for the diffusion of sulfate ion (Figure 4-8) compares very well to the concentration-distance curve for the diffusion of dissolved copper (Figure 4-5) when both curves represent the same time period. Both curves have the same

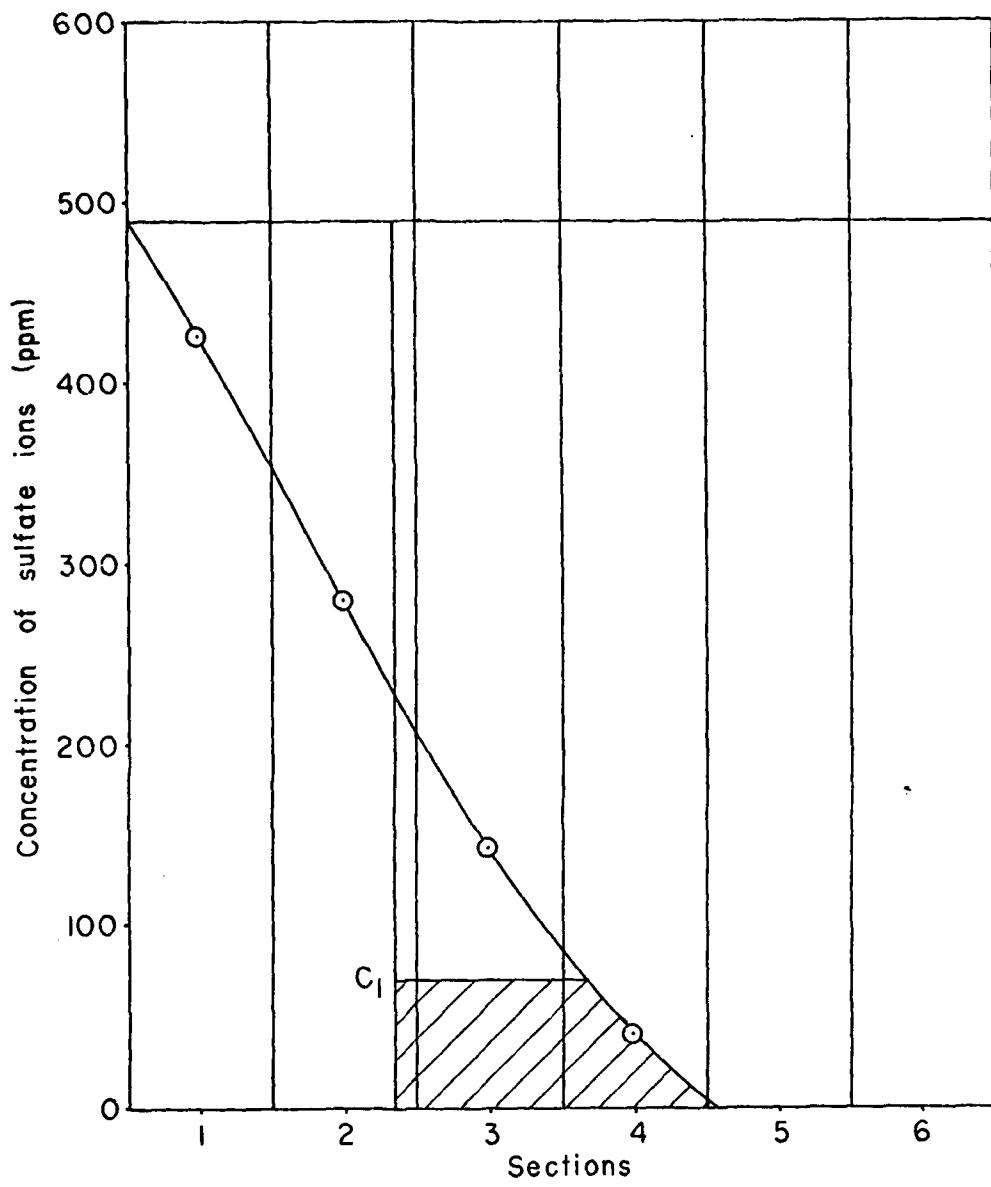


Figure 4-8. Concentration-distance curve for diffusion of sulfate ion; $t = 5$ days. The data points on this curve are from one experimental run only.

shape, although their slopes do not appear to be the same. The difference in slopes is accounted for by the fact that the concentration scales are not comparable. The slopes would be the same if the y-axis represented molarity or the percent of ion concentration present in Section 1 compared to time $t = 0$. A significant similarity between the diffusion of dissolved copper and sulfate ion which does show on Figures 4-5 and 4-8 is the fact that the leading edge of diffusing ions appears to reach the same point in time $t = 5$ days.

The diffusion coefficient for sulfate ion was calculated graphically from the concentration-distance curve on Figure 4-8. The value of C_1 was chosen at the same molar concentration as the C_1 value of copper on Figure 4-5 because both figures were based on the same experimental run. The apparent diffusion coefficient for sulfate ion derived from Figure 4-8 is $0.91 \times 10^{-5} \text{ cm}^2/\text{sec}$ at a concentration of 0.79×10^{-3} moles/liter.

The amount of uncertainty in the value of the diffusion coefficient of sulfate ion is an estimate based on the error value for $D_{\text{Cu}^{2+}}$. A graphical determination of the error in the diffusion coefficient of sulfate was not feasible because not enough data were available. However, there are several strong analogies between the copper and the sulfate determinations. The analytical technique for copper has an error value of ± 2.0 ppm, and the sulfate analysis has an error value of ± 1.5 ppm. The concentration-distance curves for the diffusion of copper and sulfate are nearly identical. The estimate of the error inherent in the graphical

determination of the diffusion coefficient for sulfate ion is, therefore, $\pm 0.09 \times 10^{-5} \text{ cm}^2/\text{sec.}$

4-4-1-3. Electrical Balance in Diffusion

The literature on diffusion generally reports on the diffusion of electrolytes in their compound form (Hodgman, 1963; Woolf and Hoveling, 1970; Awakura and others, 1975; Ahn, 1976). This is interesting in that electrolytes in aqueous solution form ions which are free to move and react independently. In this section I propose that although oppositely charged ions from an electrolytic compound may diffuse at very similar rates, the ions are not identical and the rates should be reported individually. Bockris and Reddy (1970) discuss the differences in the rate of diffusion of oppositely charged ions from a theoretical standpoint. They state that positive ions generally diffuse at a greater rate than negative ions, but they cite no specific examples.

The experimentally derived diffusion coefficient for copper is two percent greater than that for sulfate ion (Table 4-4). This fact cannot, by itself, be considered significant because of the uncertainty of the values of the diffusion coefficients. However, if the relative order of magnitude is correct, it means that for equal concentration gradients, the flux of copper should be greater than the flux of sulfate. Table 4-5 shows an analysis of the 5-day diffusion experiment. Section 1, which initially held equal concentrations of copper and sulfate, did indeed show a smaller concentration of copper than sulfate after diffusion was allowed to proceed for 5 days. The difference was two percent.

Table 4-4. Apparent diffusion coefficients of Cu^{2+} and SO_4^{2-}

Ionic Species	Concentration (moles/liter)	$D \times 10^{-5}$ (cm ² /sec)
Cu^{2+}	0.79×10^{-3}	0.93 ± 0.09
SO_4^{2-}	0.79×10^{-3}	0.91 ± 0.09

The values reported above for D represent the apparent diffusion coefficients calculated from a single experimental run where diffusion was allowed to proceed for 5 days.

Table 4-5. Analysis of 5-day diffusion experiment.

Frozen Tube Section*	pH	Positive ions	Conc. of pos. ions (meq/l)	Negative ions	Conc. of neg. ions (meq/l)
#1	3.83	Cu^{2+}	8.62	SO_4^{2-}	8.82
		H^+	$\frac{0.15}{8.77}$	OH^-	$\frac{0.00}{8.82}$
#2	4.53	Cu^{2+}	5.77	SO_4^{2-}	5.83
		H^+	$\frac{0.03}{5.80}$	OH^-	$\frac{0.00}{5.83}$
#3	5.50	Cu^{2+}	3.09	SO_4^{2-}	2.99
		H^+	$\frac{0.00}{3.09}$	OH^-	$\frac{0.00}{2.99}$
#4	5.70	Cu^{2+}	1.08	SO_4^{2-}	0.89
		H^+	$\frac{0.00}{1.08}$	OH^-	$\frac{0.00}{0.89}$

* Refer to Figure 4-2 for an illustration of the numbered frozen tube sections.

This fact is significant because the uncertainties in the analyses are too small to affect this figure. Compared to the initial concentrations of the ions in Section 1, after 5 days 44% of the sulfate remained and 45% of the copper remained.

The charge balance between the positive and negative ions in each section agrees quite well (Table 4-5). In Sections 1 and 2 the agreement of charge balance is aided by the presence of hydrogen in quantities large enough to register in the second decimal place of concentration. This suggests that not only may the oppositely charged ions from an electrolytic compound diffuse at different rates, but that the localized charge balance may be maintained by adjustments in the hydrogen ion concentration. Such a conclusion is further supported by viewing the spectrum of pH values throughout the diffusion path (Table 4-5). The original pH in Section 1 at time $t = 0$ was 4.50, so the pH of 3.83 at time $t = 5$ days represents an increase in hydrogen ion activity of 4.7 times. Also, the selective decrease in copper concentration does not appear to be the result of some unrecognized interaction with the sand; if that were the case, the relative decrease in copper would probably be the same in each cell along the diffusion path.

The study of diffusion, reported above, was secondary to the main purpose of this project, but the results offer some interesting possibilities. The fact that different ions from a single compound diffuse at different rates seems only logical, but diffusion of electrolytes is usually reported in the literature for compounds only. This is probably a consequence of the inability of most

techniques to separate the effects of individual species. In giving us the ability to measure individual species, the frozen tube method may offer an advance in the study of ionic transport phenomena.

4-4-2. Electrochemical Removal of Dissolved Copper - Time Study

This set of experiments is important because it relates directly to the purpose of the study. These experiments show that dissolved copper can be removed from a solution filling the pore spaces of a granular matrix by applying an electrical potential. The data presented here include the percentage of copper removed, together with the amount of electrical current expended to achieve that removal. Even in this simple model system these data show that the potential for using the electrochemical technique for removing copper from a saturated porous medium is worth pursuing.

The frozen tube experiments involve the application of an electrical potential across the porous medium. This requires the installation of electrodes in the tubes. Platinum was used as the electrode material in all experiments. The electrodes were cut from a sheet of platinum in the shape of a square one centimeter on a side with a thin leader extending from the square for the purpose of making the electrical connection. The platinum squares were installed at each end of the six inch long acrylic tube with one surface flat against the plexiglas sealing disc. Figure 4-1 is a photograph of a frozen tube ready for experimentation. The photograph shows the leaders extending from each end of the tube

so that the electrical potential can be applied across the tube. The manner of installation gave each electrode an effective area of one square centimeter.

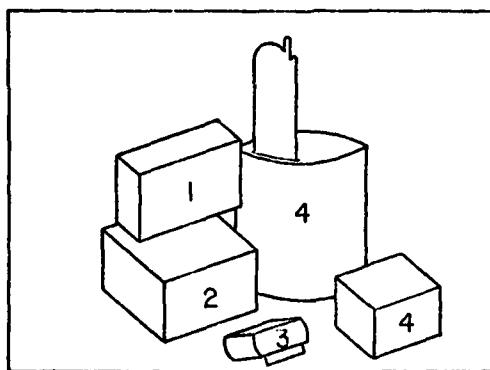
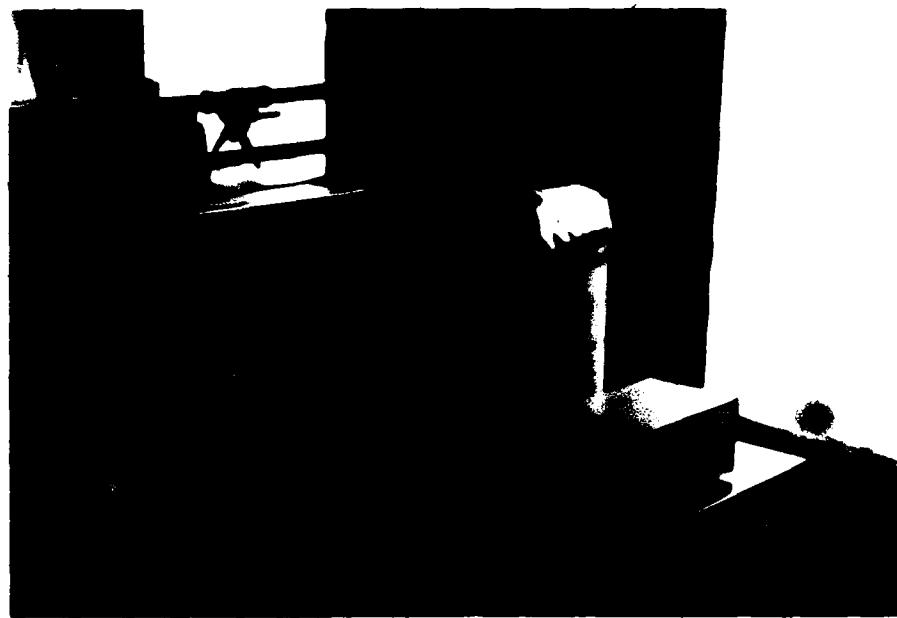
In this experiment the fluid was an aqueous solution of copper sulfate with an approximate concentration of 0.01 molarity. This extremely simple solution was used so that a model of ionic transport could be developed.

The experimental procedure consisted of applying a constant 2.50 volts direct current potential between the platinum electrodes for a set amount of time. Figure 4-9 contains a photograph of an experiment in progress showing the configuration of all of the equipment required. The amount of time of each experiment was varied. Since the voltage is sufficient to reduce dissolved copper from solution to the native state at the face of the cathode, the removal of copper from solution is accomplished.

The termination and analysis of each time study experiment was the same as all other frozen tube runs. Each one-inch section of the tube was analyzed to measure the departure from the initial uniform conditions which existed.

4-4-2-1. Copper Removal Data

The application of a constant direct current potential across the saturated porous medium did, in fact, cause a significant departure from the initial uniform conditions of the saturating solution. In each experiment the resulting copper concentrations in each section of the tube were plotted on a graph to form what will be called here a "removal curve." The removal curves which



- 1 - coulometer
- 2 - power supply
- 3 - multimeter
- 4 - temperature-controlled water bath

Figure 4-9. Photograph of an experiment in progress for the electrochemical removal of dissolved copper from a saturated porous medium. The accompanying diagram identifies the pieces of equipment in the photograph.

represent the different amounts of time that the experiments were run form a unique family of curves. This family of curves is presented on Figure 4-10. When examining these curves it should be kept in mind that the cathode was at the end of Section 1 and that the anode was at the end of Section 6. The vertical axis of this graph represents the percent of dissolved copper which remained in solution after the experimental run was completed. The initial uniform concentration across the tube is shown by the 100 percent line across the top of the graph. The actual initial concentration of the 100 percent line was 617 ppm copper in each experiment.

In general, normal expectations were realized. Dissolved copper was reduced to the native state at the surface of the cathode so the concentration of dissolved copper was sharply reduced in Section 1. The removal of copper from solution at a point resulted in a gradient of concentration toward that point. In Figure 4-10 the area under each curve represents the total dissolved copper remaining in solution at the end of the experimental run. These curves show that as time increased the amount of copper removed from solution also increased.

The mechanisms of ionic transport are apparent in the shape of the individual curves. The mechanism of ionic mobility moves the positively charged copper ions toward the cathode. The mechanism of diffusion moves ions down whatever gradient may exist; in other words, ions always move from an area of higher concentration to an area of lower concentration. In Tube Section 6 the

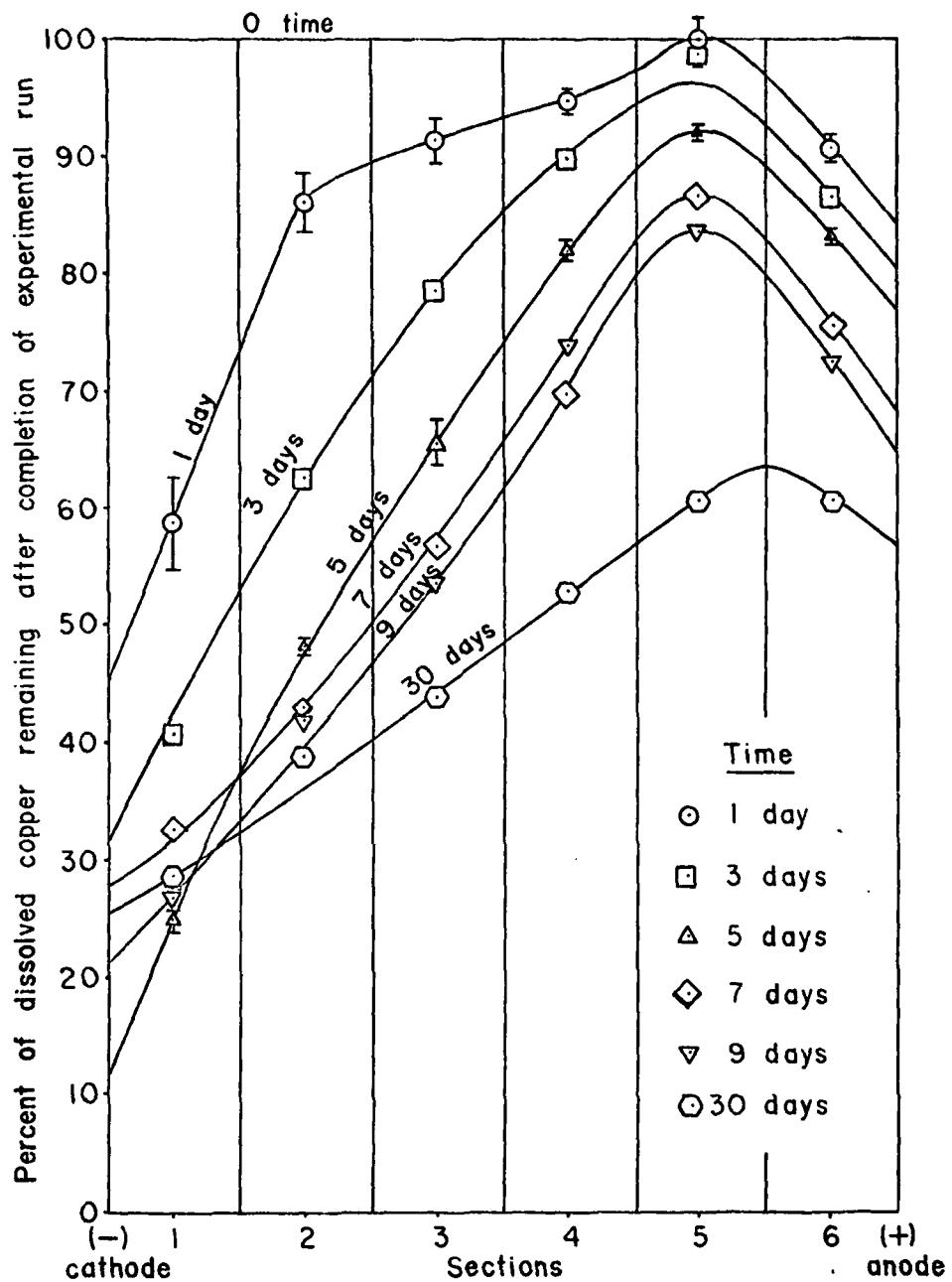


Figure 4-10. Removal curves for dissolved copper - time study. Two experimental runs were made each for the 1-day and the 5-day curves; the error bars represent the value obtained for each run. All other curves represent a single experimental run. The 100% line represents 617 ppm dissolved copper.

mechanism of ionic mobility and diffusion are working against each other. The repulsion of the anode causes the copper ions to move away from the anode and create a concentration gradient toward the anode. Diffusion then causes copper ions to move back down gradient toward the anode. The family of curves in Figure 4-10 shows that these opposing mechanisms quickly reach a state of equilibrium which is little changed through time.

One of the interesting features of the removal curves in Figure 4-10 is that there is a point of peak concentration in between the two electrodes. This peak is generally located in Section 5. The existence of this peak means that the mechanism of diffusion is causing the movement of ions in two opposite directions within the tube. This peak also divides the overall copper ion transport picture into two systems. The condition of opposing mechanisms which exists in Section 6 has already been discussed. The situation in Sections 1 through 4 will be discussed next.

In Sections 1 through 4 all positively charged ions are moving in the same direction, toward the cathode at the end of Section 1. The two mechanisms of ionic transport at work in this system are both contributing to this movement. Ionic mobility causes the positively charged copper ions to be attracted to the cathode. The removal of dissolved copper from solution by reduction at the cathode creates a decreased concentration of copper at the cathode, so diffusion also drives copper ions toward the cathode in Sections 1 through 4.

The shape of the 1-day removal curve has a feature not found in the other curves. There are two distinct limbs of the curve in Sections 1 through 4. One can only speculate about the causes of this unique feature. It is possible that copper is initially removed from solution faster than the mechanisms of ionic transport can supply dissolved copper to the cathode. By 3 days the supply process has caught up because the removal rate has become slower. Another possible explanation is that the two limbs of the curve represent the two mechanisms of ionic transport. By 3 days the dominant mechanism is in control of ionic transport in Sections 1 through 4.

The lowest average concentration in Section 1 is about 25% of the initial concentration. The initial concentration in the tube was 617 ppm copper. This is a relatively high copper concentration, and it constitutes a considerable reservoir for the mechanisms of ionic transport to draw from. After the average concentration of copper in Section 1 reaches 25 to 30 percent, dissolved copper can be supplied to the cathode fast enough to maintain this concentration for at least the 30 days of my longest experiment. This is shown by the relatively constant values of 25 to 30% in Section 1 of Figure 4-10. This situation is probably aided by a decrease in the rate of removal of copper with time.

The family of curves in Figure 4-10 definitely indicates a change in the rate of removal of dissolved copper with time. The rate of removal is initially quite rapid but steadily decreases with time. One factor which may be affected by this change in rate is

the reproducibility of the removal curves. The 1-day and the 5-day experiments were each run twice. The error bars on these two curves on Figure 4-10 show the results of the redundancy. The reproducibility is greater for the 5-day run than for the 1-day run. This may be because the rate of change is greater at 1-day so smaller differences in the two 1-day experiments result in wider differences in the outcome.

Data pertaining to the rate of removal of dissolved copper from solution as well as other parameters pertinent to this study are presented in Table 4-6. The other parameters of interest are total coulombs expended on each experimental run and current efficiency for each experiment. These data are also presented graphically in Figures 4-11, 4-12, and 4-13. Each set of data will be discussed individually.

The amount of uncertainty in the values of percent copper removed was calculated only for the 1-day and the 5-day time periods. This is because duplicate runs were made for these time periods so the amount of uncertainty accounts for the deviation between two runs as well as the error caused by the analytical technique. The amount of uncertainty was not calculated for the other time periods because the reported values of percent copper removed were based on single experimental runs. The amount of uncertainty for a single run would only account for deviations caused by the analytical technique. The uncertainty values reported in Table 4-6 represent one standard deviation.

Table 4-6. Copper removal data - time study

Time (days)	Percent Cu removed	Total coulombs expended	Current efficiency (%)
1	12.5 \pm 1.8	3.331	74.2
3	23.6	7.400	62.5
5	34.1 \pm 0.8	8.195	80.5
7	38.5	12.078	61.9
9	41.8	13.374	61.0
30	52.7	28.413	36.3

The change in the rate of removal of dissolved copper from solution is best shown in Figure 4-11. In this figure the percentage of removal is plotted against time. Starting at the intersection of the two axes, a smooth curve can be drawn through the data points. The rate of removal of copper at any point in time would be the slope of a tangent to the curve at that time. The decrease in the slope of the tangent lines shows the reduction in rate of removal with increasing time. The valuable information gained from Figure 4-11 is that the rate of removal of copper is very small at 30 days for the static system represented by this experiment. Figure 4-13 demonstrates that increased time of removal is less productive.

The expenditure of electricity versus time is plotted on Figure 4-12. The rate of expenditure of electricity appears to become fairly linear after about 7 days. This means that

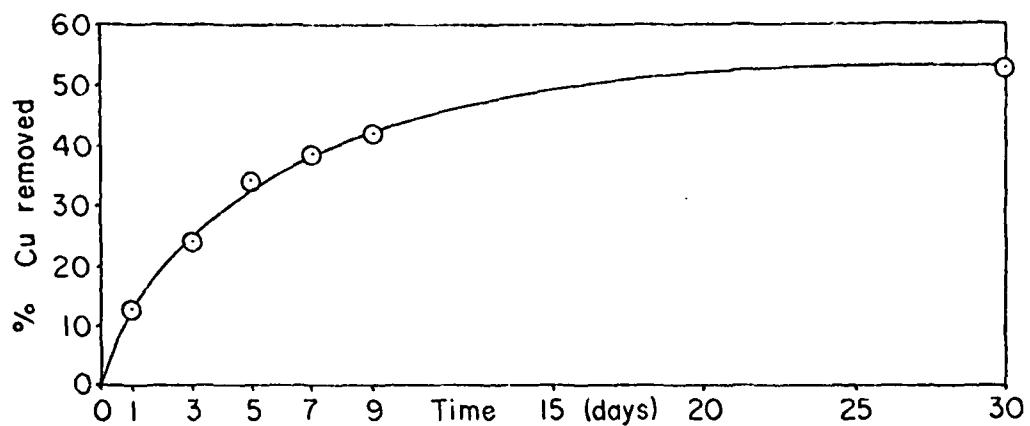


Figure 4-11. Percent copper removed vs. time.

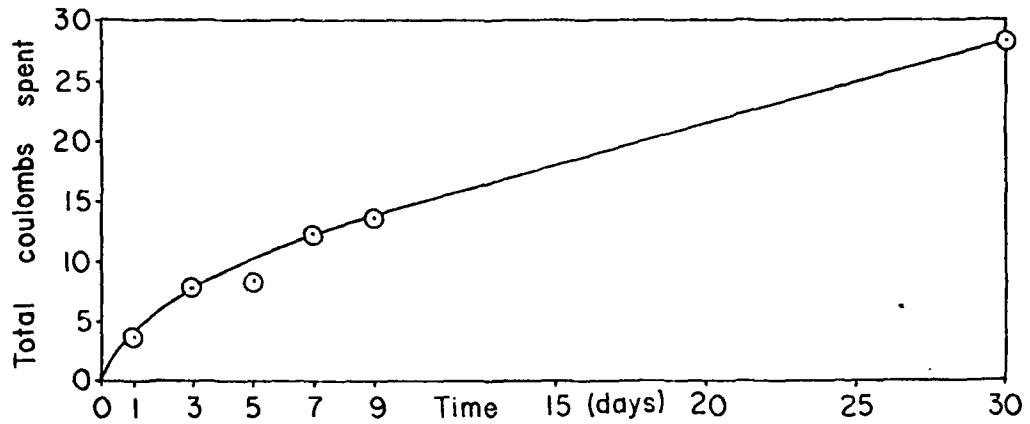


Figure 4-12. Total coulombs expended vs. time.

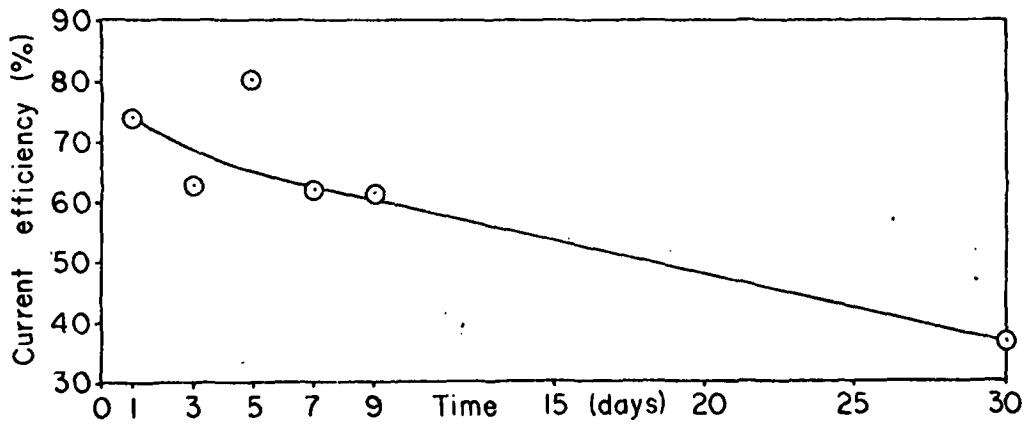


Figure 4-13. Current efficiency vs. time.

electricity continues to be spent at a fairly constant rate even though the return on that investment, that is, the rate of copper removal, decreases considerably. The optimistic side of this investment is that the total amount of electricity spent is very small. At the end of 9 days a total of 13.374 coulombs of electricity have been used. An expenditure of 13.374 coulombs at 2.50 volts potential equals only 9.29×10^{-6} kilowatt-hours, the units of which electricity is sold commercially. How this laboratory experiment would relate to a field situation and how much it would cost will be discussed later.

A plot of the data points for current efficiency versus time is shown on Figure 4-13. These points do not all fall on a smooth curve like the other data points. The useful generalization that can be made, however, is that current efficiency decreases with time. The most significant deviation from the curve is the current efficiency of 80.5% for the 5-day experiment. This high current efficiency correlates to a slightly low value for total coulombs spent for the 5-day experiment. The only explanation that seems reasonable is that the condition of the surface of the platinum electrodes varied enough from one run to the next to account for the fluctuating current efficiency values. Prior to some of these experiments the platinum electrodes were cleaned with a powdered glass and glycerin mixture or with concentrated nitric acid, but the data are not available to identify which cleaning method was used or before which experiments they were used.

Another parameter of interest, current density, can be derived from these experiments. In the system used for these experiments current density is also a function of time, decreasing as time increases. A typical current versus time curve is shown on Figure 4-14. The current density is easy to calculate from this curve since the electrodes were very close to one square centimeter each. In the 5-day experiment the current density varied from 46 to 11 microamps/cm². This is considerably less than the values recommended for industrial electroplating. A value for current density commonly used for commercial electrorefining is 20 amp/ft² (2.5 milliamps/cm²) (Smith and others, 1979) which is three orders of magnitude larger than that used in the experiments reported here. However, in these experiments the current is controlled by the environment and system of operation. In the experimental system the voltage is maintained at a constant value. As the dissolved copper is removed from solution by reduction at the cathode, the resistance to the flow of electrical current is increased. Therefore, according to Ohm's law, Equation (2-38), the current decreases as time increases.

4-4-2-2. Response of Sulfate

Sulfate was the only major anion present in solution in this experiment. The sulfate ions responded sharply to the application of the direct current potential, but the response of sulfate was different and apparently independent of the response of dissolved copper. Sulfate ions were not changed by a redox reaction at either electrode.

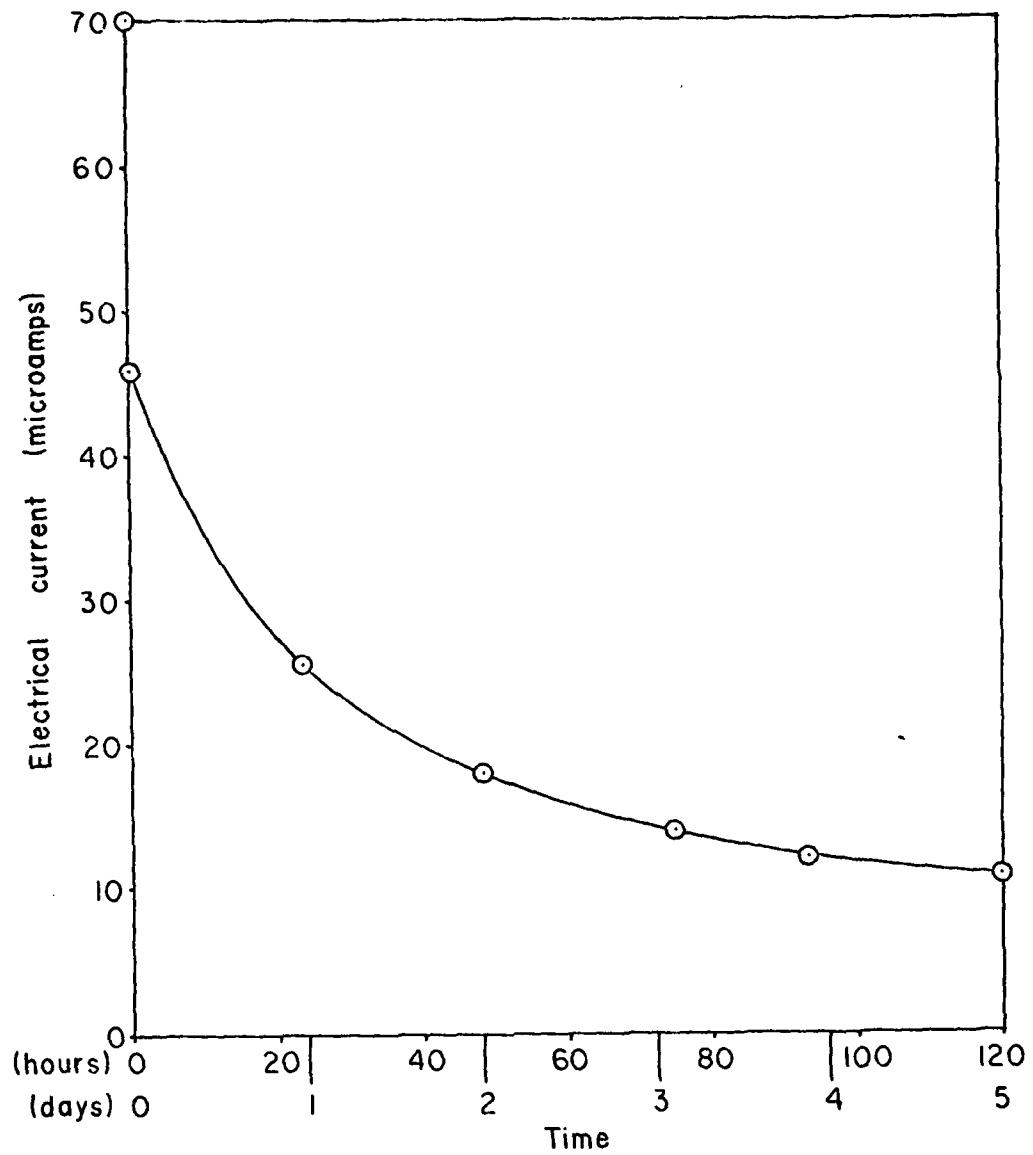


Figure 4-14. Current vs. time for an experiment on the electrochemical removal of dissolved copper - time study; $t = 5$ days.

The response of sulfate ions to the direct current potential of 2.50 volts is shown graphically in Figure 4-15. The initial uniform distribution of sulfate ions throughout the tube is represented by the horizontal line at 925 ppm sulfate. The cathode was at the end of Section 1 and the anode was at the end of Section 6. After the 2.50 volts potential was applied for 5 days, a distinct concentration gradient of sulfate ions developed. This concentration gradient is represented by the line through the circled dots on Figure 4-15. The circled dots are the actual data points for this experiment.

The concentration gradient which develops in this system is linear. The ionic transport situation is similar to that which exists in Section 6 of the copper removal curves, Figure 4-10. In other words, the movement of sulfate ions is taking place in two opposite directions as a result of two mechanisms of transport. The concentration gradient is developed as a result of the ionic migration of the negatively charged sulfate ions toward the anode under the influence of the electrical potential. At the same time, sulfate ions are diffusing away from the anode as a result of the concentration gradient which has been established. It is uncertain whether an equilibrium condition between these two opposing mechanisms was created in the 5-day time period.

When the two processes of ionic transport are at equilibrium, the concentration gradient should theoretically be linear (Bockris and Reddy, 1970). Even though diffusion is one of the processes at work here, the concentration-distance curve will be linear and

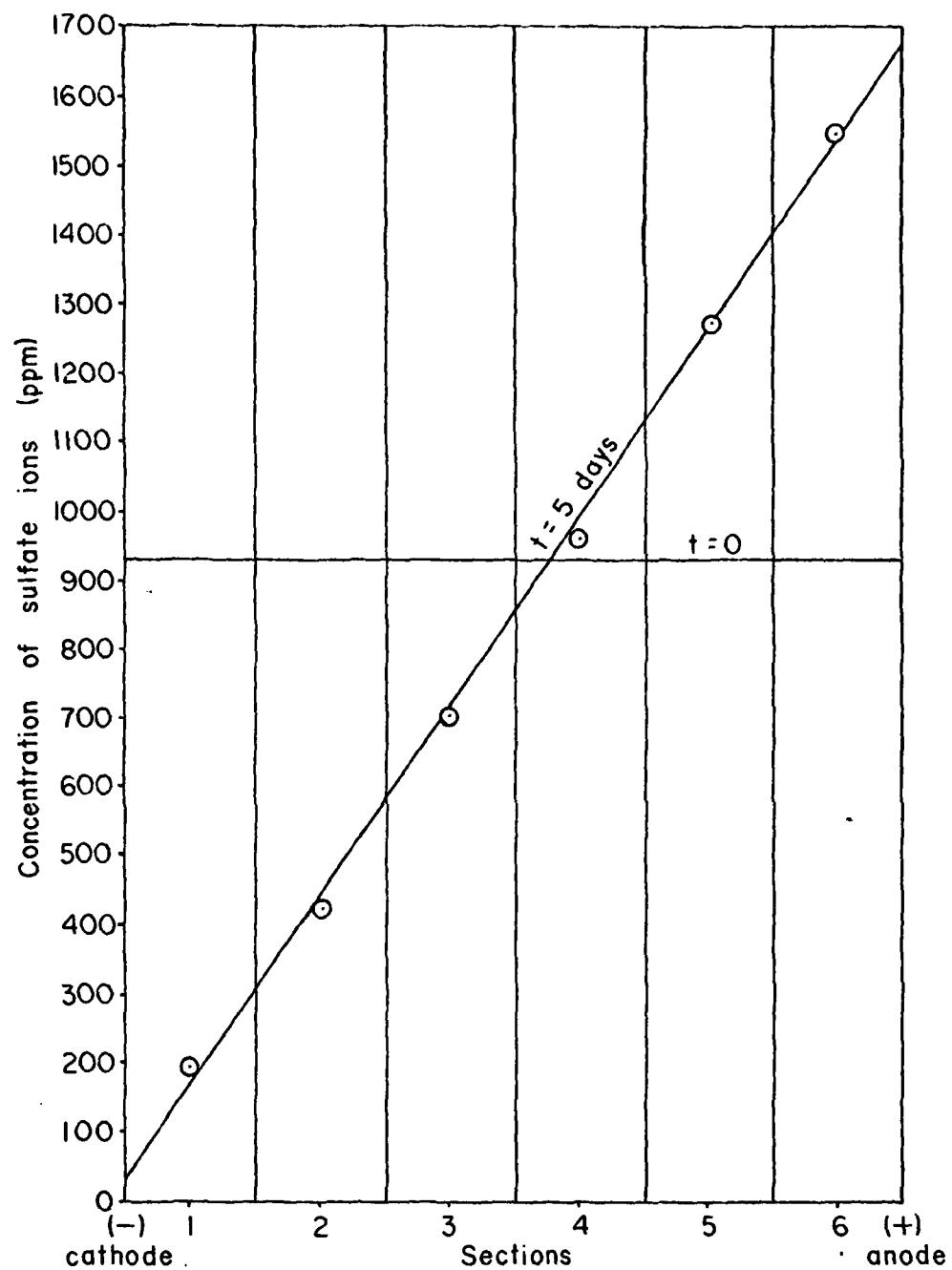


Figure 4-15. Response of sulfate ions to a direct current potential of 2.50 volts; $t = 5$ days.

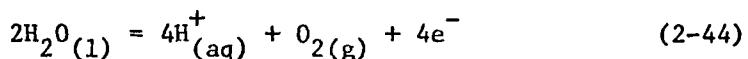
not the S-shaped curve resulting from diffusion alone as shown previously. In the experiments where diffusion was operating alone, the transport had to be described by Fick's second law because the concentration at any given point changed with time. In the situation existing in this experiment, the diffusion flux can be described by Fick's first law because the concentration of sulfate ions in the tube changes only with distance and not with time once equilibrium is achieved. Fick's first law describes a linear concentration-distance curve.

4-4-2-3. Electrical Balance in the System

The response of each of the two major ions in this system to the externally imposed electrical potential was different and apparently independent of each other. However, like the diffusion experiment, a pH gradient was also developed in this experiment. The adjustment of pH appears to maintain the local electrical balance. Table 4-7 shows the analysis of one of the 5-day experiments for the electrochemical removal of dissolved copper from solution. It should be pointed out that three different analytical techniques were used to produce this data, and that each technique has its own inherent errors. Copper concentrations were determined colorimetrically using a spectrophotometer to an accuracy of ± 0.06 meq/l. Sulfate concentrations were determined volumetrically using a titration to an accuracy of ± 0.03 meq/l. Hydrogen ion activity was measured with a pH electrode and meter, and the

activity value was converted to concentration using published activity coefficient data. These procedures were discussed in more detail in Section 4-3.

The change in pH along the tube was not necessarily the spontaneous response to the electrical imbalance between dissolved copper and sulfate ions. At the same time as dissolved copper was being reduced at the cathode at the end of Section 1, oxygen gas may have been generated at the anode at the end of Section 6. The most likely reaction which would take place at the anode is shown below (Raub and Müller, 1967, p. 42).



The evidence to support this proposition is an observation made on an experiment reported in Section 3-2-3. Bubbles of gas formed on the anode in a bulk solution of copper sulfate at the same time as native copper was being deposited on the cathode. This reaction would lower the pH in the area immediately surrounding the anode. The hydrogen ions thus produced at the anode could simply move away from the anode to cause the pH gradient along the tube. Both ionic mobility and diffusion would transport the hydrogen ions away from the anode.

The generation and movement of hydrogen ions appear to be important in this encapsulated system. The overriding requirement is that electrical neutrality must be maintained at all points in the system regardless of the mechanism which accomplishes this.

Table 4-7. Analysis of 5-day copper removal experiment

Section	pH	Positive ions	Conc. of pos. ions (meq/l)	Negative ions	Conc. of neg. ions (meq/l)
Cathode					
#1	4.44	Cu^{2+}	4.58	SO_4^{2-}	4.07
		H^+	$\frac{0.04}{4.62}$	OH^-	$\frac{0.00}{4.07}$
#2	3.97	Cu^{2+}	9.25	SO_4^{2-}	8.79
		H^+	$\frac{0.12}{9.37}$	OH^-	$\frac{0.00}{8.79}$
#3	3.24	Cu^{2+}	13.10	SO_4^{2-}	14.61
		H^+	$\frac{0.65}{13.75}$	OH^-	$\frac{0.00}{14.61}$
#4	2.67	Cu^{2+}	15.96	SO_4^{2-}	19.88
		H^+	$\frac{2.43}{18.39}$	OH^-	$\frac{0.00}{19.88}$
#5	2.13	Cu^{2+}	17.87	SO_4^{2-}	26.49
		H^+	$\frac{8.54}{26.41}$	OH^-	$\frac{0.00}{26.49}$
#6	1.87	Cu^{2+}	16.27	SO_4^{2-}	32.11
Anode		H^+	$\frac{15.84}{32.11}$	OH^-	$\frac{0.00}{32.11}$

In this experiment to remove dissolved copper from solution, as well as in the diffusion experiment, hydrogen ions appear to be the key to localized electrical neutrality.

4-4-3. Electrochemical Removal of Dissolved Copper - pH Study

These experiments expand the study of the electrochemical removal of copper by changing a different variable, pH. The pH of the different copper sulfate solutions was varied by adding sulfuric acid. The time that all of these experiments were allowed to run was fixed at 5 days. All of the physical and electrical factors remained the same as in the previous experiments.

The test solutions used in these experiments started out the same as the solutions used in the previous experiments. Initially a solution containing approximately 0.01 molarity dissolved copper was prepared by dissolving anhydrous copper sulfate in deionized water. Then the different test solutions were made by taking portions of the stock solution and acidifying each to a desired pH with sulfuric acid.

The purpose of running these experiments was to determine if copper removal could be enhanced by acidifying the solution in a saturated porous medium. The industrial copper plating process is performed in a copper sulfate bath acidified with sulfuric acid (Ollard and Smith, 1964). However, a major dissimilarity exists between the industrial copper plating process and these experiments. The plating bath is continually stirred in the industrial process, but the fluid remains static in these experiments.

The removal curves for the pH study are shown on Figure 4-16. As in all of the experiments where an electrical potential is applied, the cathode is at the end of Section 1 and the anode is at the end of Section 6. The removal curves record the deviation of the solution within the plastic tubes from the initial uniform condition. Regardless of the pH of the test solution, the copper concentration at time $t = 0$ was 615 ppm. The mechanisms of transport of the dissolved copper are the same in these experiments as they were in the time study so they need no further discussion.

As Figure 4-16 shows, the result of lowering the pH in the test solution achieved the reverse of what was desired. Lowering the pH by adding sulfuric acid decreased the amount of dissolved copper that was removed from solution. The results are a family of curves showing that this is a stepwise decrease in copper removal as the pH is lowered. The shape of the curves is generally the same though not totally uniform. An interesting anomaly is that the initial concentration of copper was exceeded in the central portion of the tube at pH = 2.0. The ionic mobility of the copper ions was sufficient enough under those conditions to allow the anode to repel the copper away from Section 6 and exceed the initial concentration in Sections 3 through 5. The reduction of dissolved copper at pH = 2.0 was not sufficient to bring the peak of the removal curve below 100 percent.

The actual percentage of copper removed as well as other pertinent data is presented in Table 4-8. No error calculations

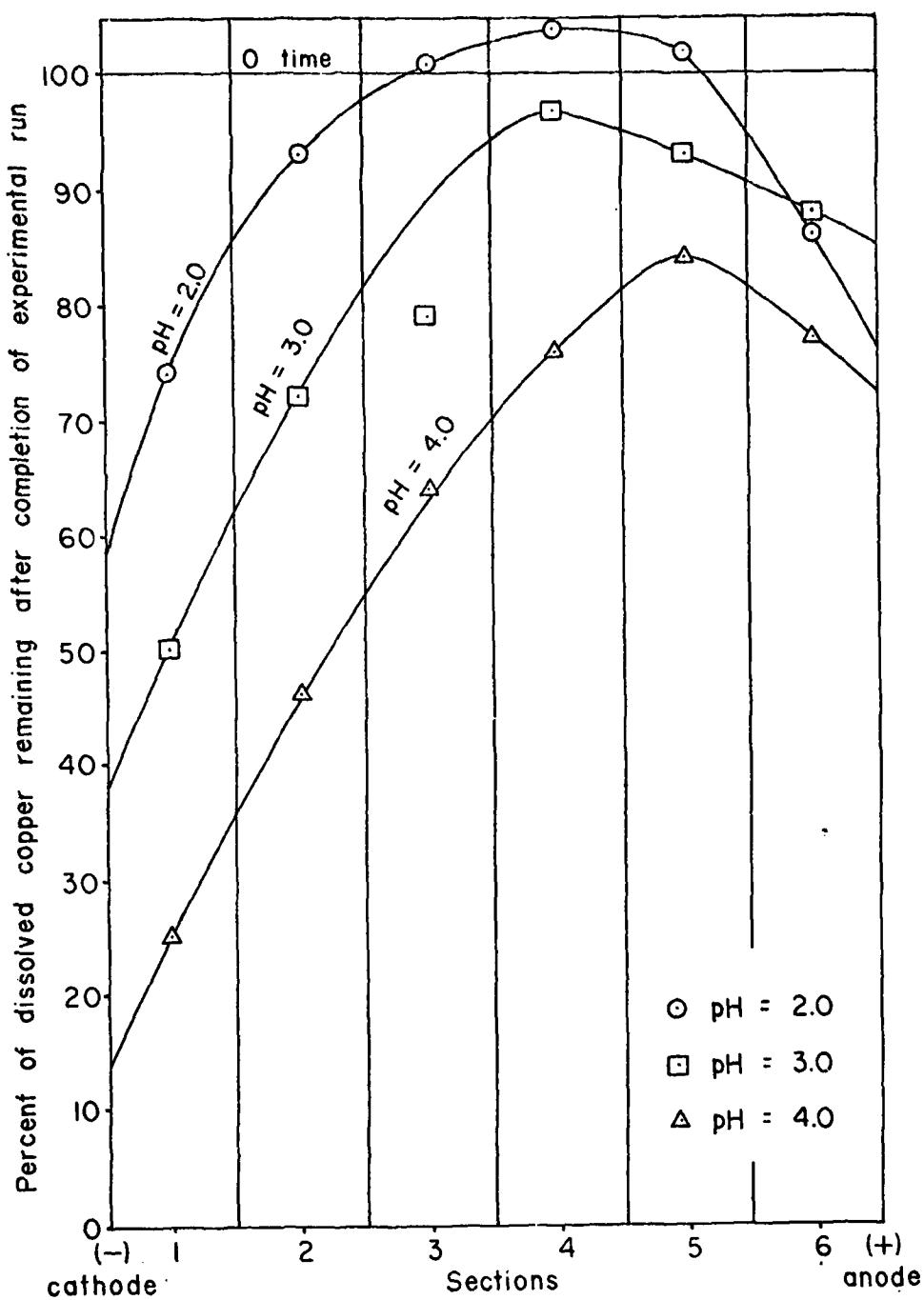


Figure 4-16. Removal curves for dissolved copper - pH study. All experimental runs were 5 days (120 hrs) long. All curves represent a single experimental run each. The 100% line represents 615 ppm copper.

were made on these data because each removal curve represents a single experimental run. Such error calculations would only reflect the amount of uncertainty in the analytical technique used for copper. These experiments are, however, probably analogous to the 5-day time study experiment in which the percent copper removed was 34.1 ± 0.08 percent. Included in Table 4-8 is the information on copper removal when no sulfuric acid had been added to the test solution and the pH was 4.5. The differences between each item of data at pH = 4.5 and pH = 4.0 do not seem significant when compared to fluctuations in the time study data in Table 4-6. The most significant factors in the data in Table 4-8 are the decrease in percent copper removed and the decrease in current efficiency with the decrease in pH. The amount of electricity permitted to pass through the system at the potential of 2.50 volts increased sharply at pH 2.0. The impact of such a depressed pH value on a commercial process of cleanup would be negative. In fact, in a commercial process the pH of the subject solution should probably be elevated to between 4.0 and 4.5.

The reason why the percent of copper removed and current efficiency decrease with decreased pH relates to the increase in the concentration of hydrogen ions in the test solution. This can be shown mathematically with transference numbers. A transference number is a dimensionless number which represents the fraction of electrical current passing through an electrolytic solution which is carried by one particular species of ion.

Table 4-8. Copper removal data - pH study

pH	Percent Cu removed	Total coulombs expended	Current efficiency (%)
2.00	7.1	33.180	4.2
3.00	20.2	9.240	42.0
4.00	37.9	9.630	76.8
4.50*	34.1 + 0.8	8.195	80.5

*No H_2SO_4 was added to this solution.

The transference number of each major ion in each test solution was calculated. Determining transference numbers requires several steps. Transference numbers are defined by the following equation (Classtone, 1942, p. 107):

$$t_i = \frac{C_i z_i u_i}{\sum C_i z_i u_i} \quad (2-54)$$

where t_i = transference number (dimensionless)

C_i = concentration (moles/liter)

z_i = valence (equivalents/mole)

u_i = ionic mobility ($cm \ sec^{-1} / volt \ cm^{-1}$).

Ionic mobility, u_i , of an ion in a solution can be determined by a very simple relationship (Robinson and Stokes, 1955, p. 42):

$$u_i = \frac{\lambda_i}{F} \quad (2-40)$$

where u_i = ionic mobility ($\text{cm sec}^{-1}/\text{volt cm}^{-1}$)

λ_i = equivalent ionic conductance ($\text{ohm}^{-1} \text{ cm}^2/\text{equiv}$)

F = Faraday's constant (96,493 coulombs/equiv).

The problem with this stepwise calculation lies in determining the equivalent ionic conductance of a specific ion in a specific solution. The limiting equivalent ionic conductance, λ_i^0 , of most ions is published in the literature, but its value decreases as its concentration in solution increases. The equations available to determine an equivalent ionic conductance of an ion in an actual solution only apply to 1:1 univalent electrolytes.

The values of equivalent ionic conductance used in this study, therefore, were determined by extrapolation. Some basic assumptions must be made in order to perform the extrapolation. We start with a fact (Glasstone, 1942, p. 56):

$$\Lambda^0 = \lambda_+^0 + \lambda_-^0$$

where Λ^0 = limiting equivalent conductance of electrolyte
($\text{ohm}^{-1} \text{ cm}^2/\text{equiv}$)

λ_+^0 , λ_-^0 = limiting equivalent ionic conductance of the cation
and the anion respectively ($\text{ohm}^{-1} \text{ cm}^2/\text{equiv}$).

The first assumption is that, as the value of the limiting equivalent conductance of the electrolyte decreases, the values of the limiting equivalent ionic conductances decrease proportionally so that each ion always conducts the same percentage of the current carried by the electrolyte. Sample calculations will be shown for pH 2.0.

The first step in the extrapolation is to estimate the value of the equivalent ionic conductance of cupric ion at 0.01 molar concentration. The equivalent conductance of copper sulfate at 0.01 molar concentration is $83.12 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv}$, and the limiting equivalent conductance of copper sulfate is $133.6 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv}$ (Harned and Owen, 1958, Table 6-2-1A, p. 697). The limiting equivalent ionic conductance of cupric ion is $54 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv}$ (Harned and Owen, 1958, Table 6-8-2, p. 231). Using our first assumption, we can calculate the equivalent ionic conductance of cupric ion at 0.01 molar concentration:

$$\lambda_{\text{Cu}^{2+}} = (54) (83.12)/(133.6) = 33.6 \text{ ohm}^{-1} \text{ cm}^2/\text{eq} \quad (4-4)$$

The second step in the extrapolation is to estimate the equivalent ionic conductance of hydrogen ion at pH 2.0. This involved calculating the hydrogen ion concentration which begins with estimating the ionic strength of the solution. Ionic strength is defined by this equation (Garrels and Christ, 1965, p. 56):

$$I_s = \frac{1}{2} \sum c_i z_i^2 \quad (4-5)$$

where I_s = ionic strength of a solution

c_i = concentration of ion i (moles/kg water)

z_i = valence of ion i (equiv/mole).

For these calculations I assume that moles/kg water equals moles/liter solution. For the estimate of ionic strength, I used $c_{\text{Cu}^{2+}} = 0.01 \text{ mole/liter}$, $c_{\text{H}^+} = 0.01 \text{ mole/liter}$, and $c_{\text{SO}_4^{2-}} = 0.015 \text{ mole/liter}$ because sulfate ion was contributed to solution by both copper sulfate and sulfuric acid.

$$I_s = \frac{1}{2}(0.01(2)^2 + 0.01(1)^2 + 0.015(2)^2) = 0.055 \quad (4-6)$$

Using this value for ionic strength, I then estimated the activity coefficient for hydrogen ion to 0.85 from Figure 2.15, p. 63 in Garrels and Christ (1965). Equation (3-4) can be used to convert hydrogen ion activity into concentration:

$$a_i = \gamma_i C_i \quad (3-4)$$

where a_i = activity of ion i (moles/liter)

γ_i = activity coefficient of ion i (dimensionless)

C_i = concentration of ion i (moles/liter).

$$C_H^+ = (0.01)/(0.85) = 0.012 \text{ mole/liter} \quad (4-7)$$

A second assumption must be made in order to estimate the equivalent ionic conductance of hydrogen ion at 0.012 mole/liter. Data for the equivalent conductance of sulfuric acid as a function of concentration were not published by Harned and Owen (1958), but they did publish this type of data for hydrochloric acid. Because the limiting ionic conductance values for sulfate ion and chloride ion are so similar,

$$\lambda_{SO_4^{2-}}^0 = 80.0 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv} \text{ and } \lambda_{Cl^-}^0 = 76.35 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv},$$

I assumed that the decrease in the equivalent conductance value per unit concentration would be the same for sulfuric acid and hydrochloric acid. The equivalent conductance of hydrochloric acid at 0.012 mole/liter concentration is estimated at $411.05 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv}$ by linear extrapolation between the published values for

0.01 and 0.02 mole/liter concentration; these values are

$\lambda_{HCl} = 412.00 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv}$ at 0.01 M and $\lambda_{HCl} = 407.24 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv}$ at 0.02 M (Harned and Owen, 1958, Table 6-2-1A, p. 697).

The estimated value of $\lambda_{HCl} = 411.05 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv}$ is $15.11 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv}$ less than the limiting equivalent conductance value for hydrochloric acid. Therefore, using my second assumption, I estimate the equivalent conductance of sulfuric acid at 0.012 molar concentration to be $414.7 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv}$, the value which is $15.1 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv}$ less than the limiting equivalent conductance value for sulfuric acid, $\lambda_{H_2SO_4}^0 = 429.8 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv}$. Since the limiting equivalent ionic conductance of hydrogen ion is $349.8 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv}$, we can now use the first assumption to estimate the equivalent ionic conductance of hydrogen ion at 0.012 molar concentration.

$$\lambda_H^+ = (349.8)(414.7)/(429.8) = 337.5 \text{ ohm}^{-1} \text{ cm}^2/\text{eq} \quad (4-8)$$

The last step in the extrapolation is to estimate the equivalent ionic conductance of sulfate ion in this solution. Because sulfate ion was contributed to solution by both copper sulfate and sulfuric acid, I estimated the concentration of sulfate ion to be 0.016 mole/liter. The equivalent conductance of copper sulfate at 0.016 molar concentration is estimated at $76.6 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv}$ by linear extrapolation between the published values for 0.01 and 0.02 mole/liter concentration; these values are $\lambda_{CuSO_4} = 83.12 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv}$ at 0.01 M and $\lambda_{CuSO_4} = 72.20 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv}$ at 0.02 M (Harned and Owen, 1958, Table 6-2-1A, p. 697). Using my first assumption, we

can calculate the equivalent ionic conductance of sulfate ion at 0.016 molar concentration.

$$\lambda_{SO_4^{2-}} = (80.0)(76.6)/(133.6) = 45.9 \text{ ohm}^{-1} \text{ cm}^2/\text{eq} \quad (4-9)$$

The stepwise process to calculate the transference numbers can now begin. The first calculation involves determining ionic mobility for each ion using Equation (2-40). The determination of the ionic mobility of hydrogen ion in the test solution of pH 2.0 is shown as a sample calculation.

$$u_H^+ = (337.5)/(96,493) = 34.98 \text{ cm sec}^{-1}/\text{volt cm}^{-1} \quad (4-10)$$

Using the values of ionic mobility for each of the ions in the test solution shown in Table 4-9, the transference numbers can be calculated using Equation (2-54). The determination of the transference number of hydrogen ion in the test solution of pH 2.0 is shown as a sample calculation.

$$t_H^+ = \frac{c_H z_H u_H^+}{\sum c_i z_i u_i} \quad (4-11)$$

$$\sum c_i z_i u_i = c_H z_H u_H^+ + c_{Cu^{2+}} z_{Cu^{2+}} u_{Cu^{2+}} + c_{SO_4^{2-}} z_{SO_4^{2-}} u_{SO_4^{2-}} \quad (4-12)$$

$$\begin{aligned} \sum c_i z_i u_i &= (0.012)(1)(34.98 \times 10^{-4}) + (0.01)(2)(3.48 \times 10^{-4}) \\ &\quad + (0.016)(2)(4.76 \times 10^{-4}) = 6.42 \times 10^{-5} \end{aligned} \quad (4-13)$$

$$t_H^+ = \frac{(0.012)(1)(34.98 \times 10^{-4})}{6.42 \times 10^{-5}} = 0.65 \quad (4-14)$$

The same procedures were followed for each of the test solutions.

The values of the transference numbers of the major ions in each test solution are presented in Table 4-9. Also presented in the table are two of the parameters required to arrive at the transference numbers.

Because of the extrapolations and assumptions required to calculate the transference numbers, the values presented in Table 4-9 must be viewed as estimates. However, these estimates are adequate to help explain the results of the experiments reported in Table 4-8. As the pH of the test solution is lowered from 4.0 to 2.0, the transference number of hydrogen ions increases from 0.02 to 0.65. This means that at pH = 4.0 hydrogen ions are only carrying 2% of the electrical current, but at pH = 2.0 the hydrogen ions are carrying 65% of the current. It is the preferential ability of the hydrogen ions at increased concentrations to carry the electrical current which accounts for the decrease in reduction of copper ions to metal.

The obvious conclusion of this set of experiments is that the effective removal of dissolved copper from a static solution in a porous medium is greatly reduced when the pH of the solution drops below 4.0. If a lower pH were encountered in a field situation, consideration of raising the pH would be necessary.

Table 4-9. Transference numbers of the ions in the pH study

pH	Ion	λ_i ($\text{ohm}^{-1} \text{cm}^2/\text{eq}$)	u_i ($\text{cm sec}^{-1}/\text{volt cm}^{-1}$)	t_i (no units)
2.0	H^+	337.5	34.98×10^{-4}	0.65
	Cu^{2+}	33.6	3.48×10^{-4}	0.11
	SO_4^{2-}	45.9	4.76×10^{-4}	0.24
3.0	H^+	344.9	35.74×10^{-4}	0.16
	Cu^{2+}	33.6	3.48×10^{-4}	0.32
	SO_4^{2-}	49.4	5.12×10^{-4}	0.52
4.0	H^+	347.8	36.04×10^{-4}	0.02
	Cu^{2+}	33.6	3.48×10^{-4}	0.39
	SO_4^{2-}	49.8	5.16×10^{-4}	0.59

4-4-4. Electrochemical Removal of Dissolved Copper - Groundwater Study

This last experiment was designed to give some indication of whether the electrochemical technique of copper removal might work in a natural environment. The removal experiment was again duplicated, but the test solution which saturated the sand was changed in two ways. A background matrix of groundwater components was added to simulate an average groundwater percolating through an unconsolidated alluvial aquifer. Secondly, the initial copper concentration was greatly reduced to more accurately resemble a natural contamination level.

The actual groundwater which served as a model for this artificial analog was a groundwater from alluvium at Mesa, Arizona (White and others, 1963, Table 11, Sample 11, p. F28). An analysis of the water from Mesa, Arizona is shown in Table 4-10. I tried to model this alluvial groundwater in two respects, components and level of total dissolved solids. The artificial groundwater was made by adding 0.420 grams of NaHCO_3 and 0.250 grams of CaCl_2 to one liter of deionized water. At this point the pH of the water was 7.70. The water was next acidified to pH 4.60 with sulfuric acid. Finally 0.150 grams of CuSO_4 was added to the liter of water. The water was acidified with sulfuric acid to simulate contamination of a groundwater by an acid mine water. The artificial contaminated groundwater which was used as the test solution in this experiment contained 59 ppm copper and a total dissolved solids concentration of 736 ppm. This copper concentration was

Table 4-10. Analysis of alluvial groundwater from Mesa, AZ*

Ion	Concentration (ppm)	Concentration (meq/l)
Ca	58	2.89
Mg	22	1.81
Na	146	6.35
K	4.0	<u>0.10</u>
Total cations		11.15
HCO_3	184	3.02
SO_4	39	0.81
Cl	255	7.19
NO_3	2.9	<u>0.05</u>
Total anions		11.07
TDS	<u>737</u>	

pH = 7.7

* White and others, 1963, Table 11, Sample 11, p. F28.

Table 4-11. Analysis of artificial contaminated groundwater

Ion	Concentration (ppm)	Concentration (meq/l)
Ca	87	4.34
Na	117	5.09
Cu	59	<u>1.86</u>
Total cations		11.29
Cl	154	4.34
SO ₄	319	<u>6.65</u>
Total anions		10.99
TDS	<u>736</u>	
pH =	4.60	

less than one tenth of the copper concentration in all other copper removal experiments. The independent analysis of the artificial groundwater by the Environmental Trace Substances Laboratory is shown on Table 4-11.

The results of applying the 2.50 volts direct current potential across a tube of sand saturated with this simulated groundwater are shown on Figure 4-17. The physical construction of this experiment is the same as the other copper removal experiments. Two experimental runs were made to confirm the results. Duplication is more important when the results represent a single curve on a graph than when a family of curves is developed which show trends resulting from the change of a single variable.

There is a remarkable resemblance between the removal curve on Figure 4-17 and the removal curve for the 5-day time study experiment, Figure 4-10. An average of 75% of the copper was removed from Section 1 in both experiments. The curves in both experiments have the same shape although the peak concentration is higher in the groundwater study than in the time study. These similarities are significant when the differences in the make-up of the initial test solutions are considered. In the time study, Figure 4-10, the initial test solution contained 617 ppm dissolved copper, whereas in the groundwater study, Figure 4-17, the initial test solution contained only 59 ppm copper. In the time study the only ion competing with copper to carry the electrical current was sulfate, but in the groundwater study several cations as well as anions were available to compete with copper for the conduction of electrical current.

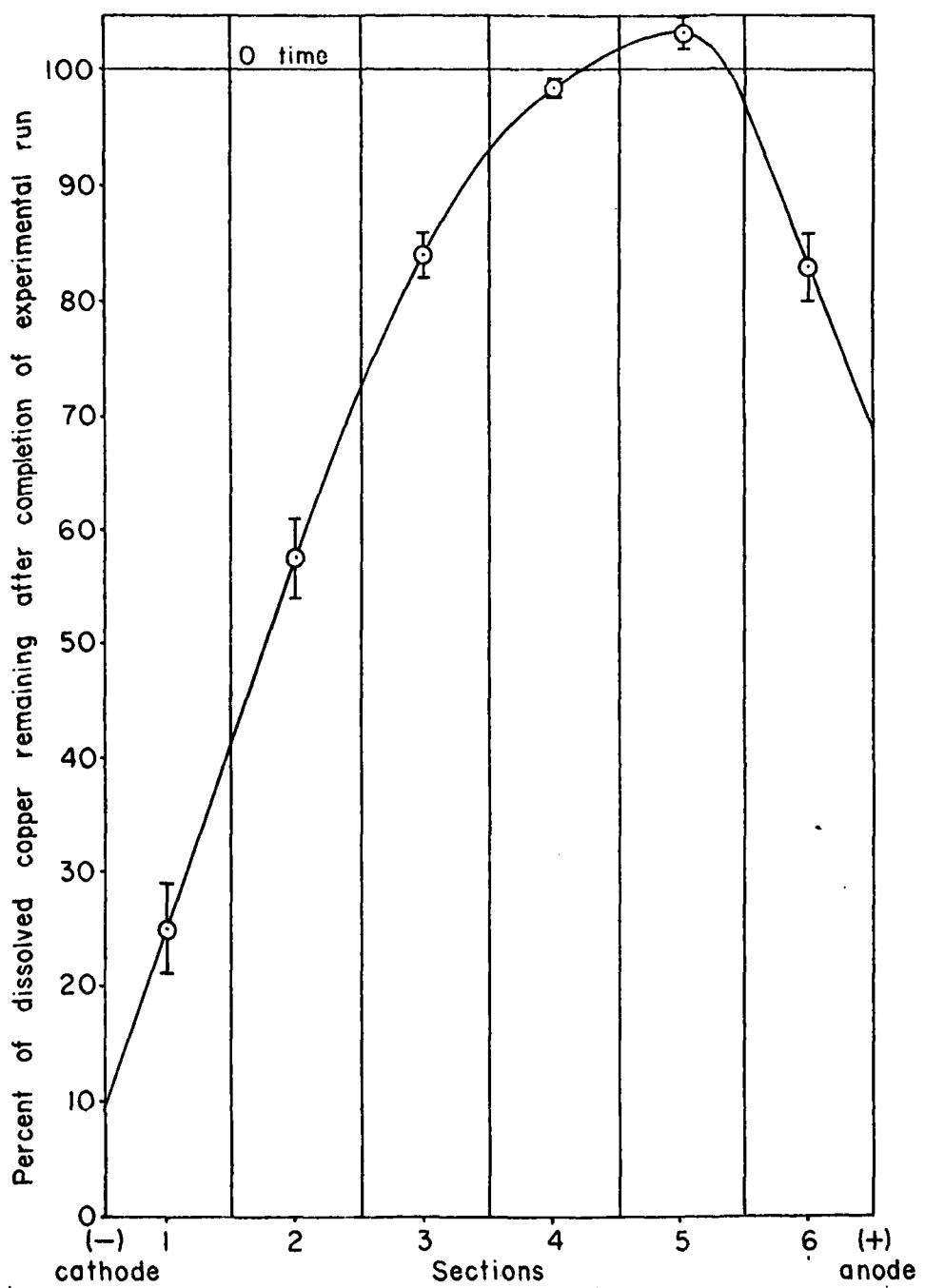


Figure 4-17. Removal curve for dissolved copper - groundwater study. The curve shown is the average of two experimental runs; the error bars represent the values obtained for each run. Both experimental runs were 5 days (120 hrs) long. The 100% line represents 59 ppm copper.

Table 4-12. Copper removal data - groundwater study

Copper conc. (ppm)	Percent Cu removed	Total coulombs expended	Current efficiency (%)
59*	25.6 \pm 3.8	5.015	9.0
617**	34.1 \pm 0.8	8.195	80.5

* from the groundwater study

** from the 5-day time study

A comparison between the copper removal data for the groundwater study and the data for the 5-day time study is shown in Table 4-12. The amount of uncertainty was calculated to reflect the deviation between two actual experimental runs as well as the error inherent in the analytical technique for copper. The amount of uncertainty in the percent of dissolved copper removed from solution is nearly five times greater when the test solution contains groundwater components and a low copper concentration, 59 ppm, than it is when the test solution contains only a high concentration of copper, 617 ppm.

The current efficiency dropped to below 10% when the test solution simulated a normal groundwater. This is because the groundwater components provide several ions other than copper to carry the electrical current. This could be quantified in terms of transference numbers as it was in the pH study, but the groundwater composition is too complex to accurately estimate equivalent ionic conductances for the various ions. However, for some

comparison it can be noted that calcium has a higher limiting ionic conductance, $59.5 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv}$, than copper, $54 \text{ ohm}^{-1} \text{ cm}^2/\text{equiv}$, and is present in this artificial groundwater at a higher concentration than copper (Harned and Owen, 1958, Table 6-8-2, p. 231). Therefore, the calcium alone will carry more current than the copper.

The percentage of copper removal from the artificial groundwater solution is 25.6%, a very encouraging fact when two points are considered: (1) the initial copper concentration was low, 59 ppm, and (2) an average of 75% of the dissolved copper was removed from Section 1. Unfortunately, the current efficiency was less than 10%. On the positive economic side of the process, considerably less total current was expended in the groundwater test than in the more concentrated time study tests.

This simple simulation of a natural environment did not, at least, invalidate the use of the electrochemical technique for removing dissolved copper from a porous medium saturated with a contaminated groundwater. Therefore, it may be concluded that this method may be feasible for field use. In fact, this experiment suggests that if several sets of electrode pairs were used in series in an environment where the groundwater was migrating very slowly past the electrodes, in a cascade, virtually all of the dissolved copper could be removed from solution. Possible field installations will be discussed later.

4-5. Summary

The following list is intended to summarize the major conclusions drawn from the experimental work performed for this study and reported in this chapter.

- (1) The frozen tube method offers a new and useful technique for studying ionic transport mechanisms.
- (2) The frozen tube method is particularly advantageous for studying ionic transport in a solution filling the pore spaces of a geological material because the opaque nature of the porous matrix, which precludes using many other methods, is not a hindrance to the frozen tube method.
- (3) Once a porous medium has been calibrated to determine tortuosity, the frozen tube method can be used to calculate diffusion coefficients.
- (4) In the experiment where the electrochemical removal of dissolved copper from a static fluid was measured at different time increments, the percentage of copper removal increased with time. However, copper removal in this system became less practical for extended periods of time because current efficiency and the rate of removal decreased with increased time.
- (5) The pH of the test solution is a very important factor in the electrochemical removal of dissolved copper. Below pH 4.0 a large proportion of the electrical current is carried by the hydrogen ions so that a smaller proportion of electricity is used to transport and reduce dissolved copper.

(6) The use of the electrochemical technique may be feasible for removing dissolved copper and other contaminants from certain polluted natural waters in some field settings.

(7) No effort was made to remove dissolved oxygen from any of the test solutions used in the experiments reported in this chapter. If dissolved oxygen was reduced at the cathode, it did not significantly decrease the removal of dissolved copper from solution by the electrochemical technique in any obvious way.

CHAPTER 5

FIELD INSTALLATION

5-1 Introduction

All of the information contained in this chapter is in the form of hypothetical proposal because no field testing was done as part of this study. Many of the ideas proposed here could lead directly to additional work.

The proposals listed here for the field installation of the electrochemical technique cover several facets of the installation process. Among these is a discussion of the geological settings where the application of this technique may be feasible. Also included are some detailed proposals for equipment configuration in different situations. Distinctly absent in this chapter is a description of equipment for electrical power supply. Only the output requirements of such machinery are listed.

5-2. Field Settings

The electrochemical cleanup technique, like any other process, will be limited in its application. First, it will be confined to the removal of heavy metal ions which can be reduced to metal at an electrode surface. This study investigated only copper. Secondly, the area that can be cleaned up is restricted more by equipment layout than anything else. Finally, the use of the

cleanup technique is limited by the geological setting of the contamination problem. Geological setting includes the properties of the porous medium involved and the movement of the saturating fluid.

It was specifically envisioned that the electrochemical cleanup technique would be used on pollution problems created by man. Although some of these can be quite massive, they are generally more restricted in area than geochemical conditions created by nature. Actually, the size of the area that can be cleaned up depends upon two factors: (1) the practical limits of equipment layout and (2) the movement of the saturating fluid. If the contaminated solution were totally stagnant, rows of electrode pairs would probably need to be installed over the entire affected property. An area of a few acres might be the limit of practicality in this case. In contrast, if the contaminated groundwater were in motion, a cleanup might be accomplished by installing only a "fence" of electrode pairs at the property boundaries. This will be discussed further in Section 5-2-1. It should be understood, however, that there is a maximum allowable rate of movement or percolation velocity of the groundwater for an electrochemical cleanup to be practical. This will be discussed in Section 5-2-2.

5-2-1. Equipment Configuration

One of the first considerations to be made concerning equipment would be the choice of a material for the electrodes. The factors affecting this decision were already discussed in Chapter 2.

Platinum electrodes were used in the laboratory tests, and they performed well, but cost would almost certainly prohibit the use of platinum electrodes in the field. The most logical choice for field use would probably be iron or aluminum or possibly graphite.

The physical configuration of the electrodes in the field would be rows of electrode pairs implanted in the porous medium. In virtually all conceivable situations several sets of these electrode pairs installed in series would be required. The term series here refers to the physical configuration of electrodes. As far as the electrical connections are concerned, the electrodes of the same polarity in a row are connected in series, and the rows are connected to each other in parallel. This is clarified in the diagram in Figure 5-1 which shows three sets of electrode pairs with the individual electrodes set in rows. Note in the diagram that the rows of electrodes are positioned perpendicular to the direction of flow of the fluid. The diagram also shows that in each electrode pair the cathode is positioned downstream from the anode.

From this general configuration of electrodes specific configurations can be created to fit the situation where they would be used. Figures 5-2a and 5-2b show schematically a two stage configuration for cleaning up a piece of property contaminated with a dissolved metal in a stagnant fluid. Stage 1 is designed to reduce the contamination on the subject property to an acceptable level. Stage 2 is meant to serve as a "fence" to remove and isolate additional contamination as it would tend to diffuse into the clean groundwater on the site. Figures 5-2, 5-3, and 5-4

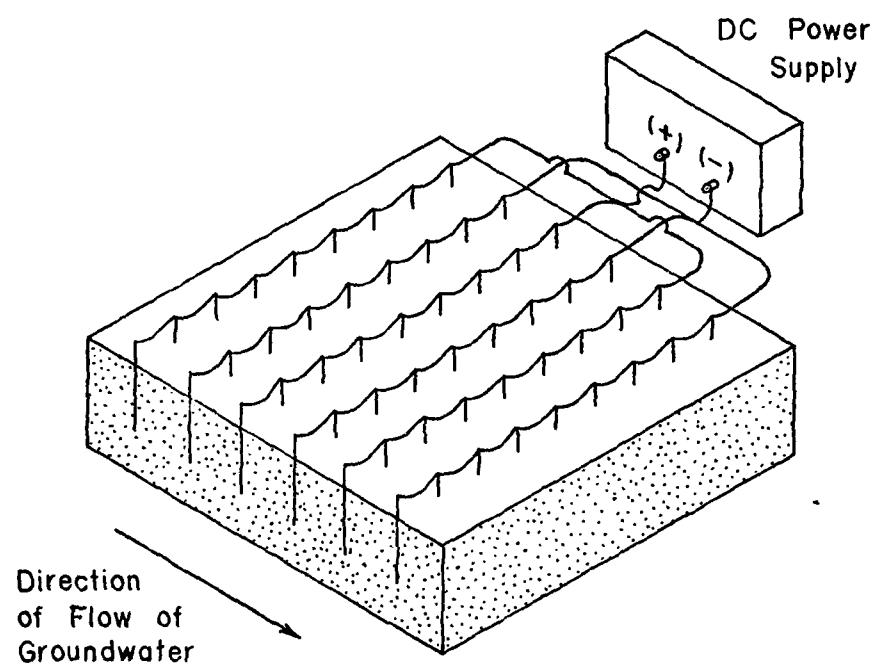


Figure 5-1. General configuration of electrodes.

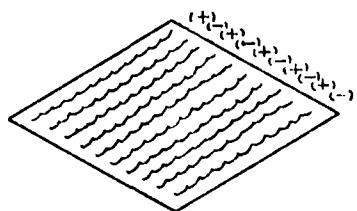


Figure 5-2a. Equipment configuration for stagnant fluid - Stage 1, Cleanup.

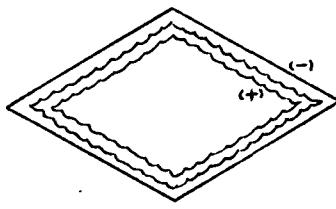


Figure 5-2b. Equipment configuration for stagnant fluid - Stage 2, Maintenance (isolation).

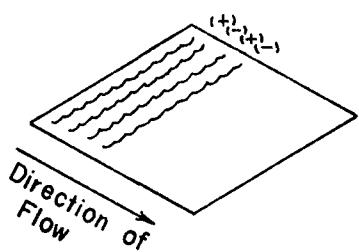


Figure 5-3a. Equipment configuration for contamination moving onto a given property.

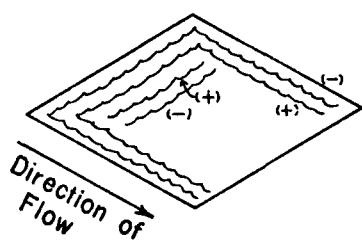


Figure 5-3b. Alternate equipment configuration for contamination moving onto a given property.

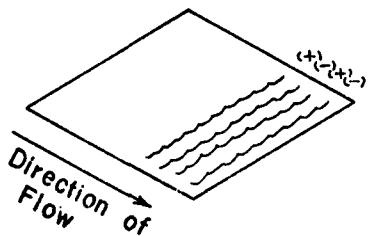


Figure 5-4a. Equipment configuration for contamination originating on a given property.

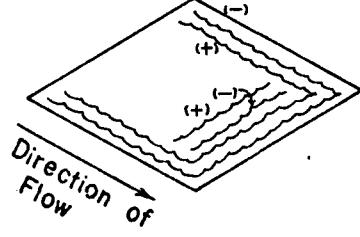


Figure 5-4b. Alternate equipment configuration for contamination originating on a given property.

should be viewed as schematics and not as exact drawings. The number of rows of electrode pairs would probably vary from one field site to the next and could not be represented in these figures.

Two different configurations each are shown which might be feasible for two different circumstances where the groundwater is in motion. Figure 5-3 is meant to protect a specific site from a contaminant which is originating elsewhere and migrating toward the site. Figure 5-3a shows a simple installation which might suffice for some specific property providing that lateral dispersion of the contaminant is not too great. The electrode distribution shown in Figure 5-3b is designed for the same purpose as the equipment in Figure 5-3a, but the layout in Figure 5-3b is slightly more extensive and probably offers the site better protection from contamination. The number of electrode pairs required along the flanks of the property would probably be less than the number required which are perpendicular to the flow of the fluid.

A second situation in which the groundwater is in motion is considered in Figure 5-4. In this situation the contamination is originating on the subject property and migrating off of the site. An industrial site or a mining operation could be such a source of pollution. The object of the equipment configurations is to prevent the pollutant from leaving the site and contaminating someone else's property. The width of the plume of contamination would determine whether Figure 5-4a or 5-4b were more appropriate. In the case of

a mining operation, the source of pollution might be fairly constant and such an installation of electrical equipment would be in place indefinitely. On the other hand, an industrial plant may have had a single batch spill of dissolved metal so that this type of equipment installation would only be required for a finite period of time.

One of the significant factors of equipment configuration deals with the spacing between electrodes. This question was not specifically answered by this study. In all of the experimental work performed in this study, the electrodes were placed six inches apart, but this spacing is probably impractical for most field situations. The question of electrode spacing is an area that requires further examination because this research did not lead to a method for extrapolation from the six-inch tubes to longer distances between electrodes. For any field site, frozen tube tests could be run using actual samples of the porous medium and varying electrode spacing. For a field situation a distance of one to three feet between electrodes would probably be the minimum practical spacing.

5-2-2. Velocity of the Fluid

The velocity of the groundwater carrying the contaminant is extremely important because it can invalidate the use of the electrochemical technique. It is possible for the fluid to flow past the electrodes so fast that virtually no dissolved metal is removed from solution by reduction at the surface of the cathode.

Defining a maximum fluid velocity is difficult and, in fact, cannot be done in any general sense. What can be done is to estimate a maximum fluid velocity permissible for each case.

There are several variables which must be specified to define an individual case. These are the same variables that were used to define the conditions of the frozen tube experiments. They are: (1) the composition of the solution, (2) the nature of the porous medium, (3) temperature, (4) electrode material, (5) electrical potential, and (6) electrode spacing.

The frozen tube experiments produce an empirical curve, called a removal curve, which shows the distribution of dissolved metal after the completion of an experimental run. It is from this removal curve that a maximum fluid velocity can be estimated. For illustration, refer to Figure 4-10, which shows the removal curves for the electrochemical removal of dissolved copper from solution as a function of time. At the end of 24 hours the concentration at the face of the electrode was reduced to below 50% of its original concentration. However, a peak concentration of 100% of the original concentration remained $4\frac{1}{2}$ inches from the cathode. If this bulk mass of the remaining dissolved copper were transported past the cathode in less than 24 hours, the flow of the fluid would overwhelm the ability of the cathode to remove the dissolved metal ions from solution. Therefore, the maximum permissible fluid velocity for the conditions which define this experiment would be estimated at 4.5 inches/day or about 11 cm/day.

This is an apparent velocity across a length of the porous medium and should not be confused with the velocity of the fluid through the pore spaces of the porous material.

5-2-3. Near-Surface Contamination

The greatest differences between equipment installations for cleaning up near-surface contamination and deeply buried contamination is in the manner in which the electrodes would be implanted. There are many more options available for electrode installation in near-surface conditions.

The first option would be simply to drive both electrodes into the ground. This is the simplest and cheapest alternative, but it is limited by at least two factors. First, one cannot drive the electrodes very deep. If the porous medium were rocky, the depth that the electrodes could be driven would be further limited. This is assuming that the electrodes are fairly light rods. The problem of depth of insertion could be overcome if the electrodes were hardened steel driven into the ground with a pile driving machine. The real objection to driving both the anode and the cathode into the ground arises when the cathode must be removed from the porous medium. If the cathode is in intimate physical contact with the porous medium, wrenching it from the ground might scrape off some of the reduced metal, leaving it in the hole. If the reduced metal remains in the porous medium, it can be redissolved later and the contamination has not been removed.

An improved method for implanting the cathode would be to drill a hole in the ground large enough to loosely insert the electrode. Drilling a hole for the cathode would overcome the problem of depth of installation. In a drilled hole the cathode would have intimate contact only with the contaminated groundwater. Installing the cathode in an unlined hole assumes that the porous medium will not cave in on the electrode during the time that the installation is expected to be required. If the porous medium is prone to cave in or if the installation is expected to be required for an indefinite period of time, the hole could be lined with a plastic well screen. In either case, an oversized hole for the cathode means that the cathode could be replaced periodically and the reduced metal could be recovered. In some cases the recovery of the reduced metal could help defray the cost of the cleanup, as in the cleanup of abandoned tailings ponds.

Another option for the installation of the electrodes would be to drill holes for both the anode and the cathode. If a drill rig is brought to the site to drill holes for the cathode, it would probably be economical to drill holes for the anode as well. However, there are probably few circumstances in which it would be worth the expense to screen the holes for the anode unless it was also being coated with some material which was desirable to remove from the site.

5-2-4. Deeply Buried Contamination

The case where one might consider using the electrochemical technique to clean up deeply buried contamination would be in a fairly thin, confined aquifer carrying a narrow plume of pollutant in a slow moving water. In this case a "fence" of rows of electrode pairs could be installed. The main problem would be expense because all of the holes would have to be drilled and probably cased and screened. Also, it seems unlikely that an exact array of electrodes could be assured at any depth because of the difficulty of drilling perfectly straight holes. In most cases deeply buried contamination would be out of the reach of electrochemical cleanup because of the expense and difficulty of the installation. It would only be considered for rare and financially important cases.

5-2-5. Cost

This section only considers the expense of operating the electrochemical cleanup and not the expense of equipment or installation. A method is shown by which the results of a frozen tube experiment can be used to calculate a minimum expenditure of current to achieve the same results in the field. This calculation assumes that the groundwater in the field is stagnant, as it was in the frozen tube experiments. The figure calculated from laboratory results would be a minimum value for field use because there are at least two places in a field installation where electrical current could be lost. First, the current efficiency of reducing metal ions

may be lower in the unconfined environment of the field than it is in the confined plastic tubes of laboratory experiments. Second, some electricity will be lost in the process of converting commerical alternating line current to low voltage direct current.

The calculation is very straightforward. The current which passes through a solution at a fixed potential is directly proportional to the area of the electrodes immersed in the solution. Therefore, one must first calculate the total area of the electrodes which is buried in the saturated porous medium. This area may be divided by the area of the electrodes used in the frozen tube experiment, and the result should then be multiplied by the total coulombs spent in the experiment. Coulombs may be converted to kilowatt-hours by the following equation:

$$\text{kilowatt-hours} = \text{volts} \times \text{coulombs} \times 2.778 \times 10^{-7}. \quad (5-1)$$

The cost of electricity varies with different utility companies and categories of service provided. In order to give some idea of the cost of electricity, information is presented in Table 5-1 on the current rates charged by the Public Service Company of Colorado for general residential service and general industrial service. The actual cost for electricity is cheaper by the industrial rate than by the residential rate, but the demand charge for industrial service is an expense not borne by the residential customer. Demand is defined as the average kilowatts used during the fifteen minute period of maximum usage during the month (Public Service Company of Colorado, 1980).

Table 5-1. Cost of electricity from Public Service Company of Colorado*

<u>General Residential Service</u>	
<u>Monthly Usage</u>	<u>Rate</u>
First 30 kilowatt-hours or less used	\$ 1.97
Next 70 kilowatt-hours used, per kwh	0.05119
Next 900 kilowatt-hours used, per kwh	0.04269
All over 1000 kilowatt-hours used, per kwh	0.03211
Monthly Minimum	\$ 1.97

<u>General Industrial Service</u>	
<u>Monthly Usage</u>	
Demand Charge:	
First 25 kilowatts of demand or less	\$220.00
All over 25 kilowatts of demand, per kwh	6.99
Energy Charge:	
All kilowatt-hours used, per kwh	0.01543
Monthly Minimum	\$220.00

*Public Service Company of Colorado, 1980, Sheets 101, 125.

For the purpose of illustration, let us assume that we have 100 square feet of cathode surface area immersed in a contaminated groundwater. The system is operating at 2.50 volts of direct current potential and an average current density of 12 microamps/cm². This would mean that we would use 2.07360 kilowatt-hours of electricity in a month (31 days). According to the rates in Table 5-1, this would cost a residential customer \$1.97 and an industrial customer \$220.03.

For a percolating groundwater the method described above for estimating the amount of electricity spent could not be used. Future work involving some type of column study should be performed. This will be discussed in the next chapter.

5-3. Conclusion

This chapter has outlined some suggestions for possible field installations of the electrochemical technique of environmental cleanup. Each section points to further study of the technique. The main conclusion that can be drawn here is that before any field utilization of the technique is attempted, the conditions unique to that site should be investigated by some laboratory testing using the frozen tube method.

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CHAPTER 6

FUTURE WORK

6-1. Introduction

As the concepts of this study were being tested and developed in the laboratory, many ideas for further work were also generated. Time did not allow the pursuit of these ideas as part of this study. Some of these ideas pertain directly to the removal of dissolved metal from a saturated porous medium and some suggest utilizing the frozen tube method to investigate other geochemical phenomena. To prevent these ideas being lost, they are listed here in the hope that some other researcher will find something worthy of his interest and begin where this study ended.

6-2. Diffusion

The frozen tube method of studying ionic transport may offer many possibilities for investigating new aspects of diffusion. The two areas suggested here are diffusion in geological materials and diffusion in complex solutions.

Diffusion in geological materials was studied in the past using the diaphragm cell method (Garrels and others, 1949). One of the problems with the diaphragm cell method is that the thin slice of rock used as the diaphragm may not be representative of the rock as a whole. The diaphragm may contain a high density of the

irregularities present in a rock formation or it may contain none of the irregularities. The frozen tube method can utilize a larger piece of rock and, therefore, a piece more representative of the whole. Also, the diaphragm cell method does not lend itself to the study of diffusion in unconsolidated materials. The frozen tube method, on the other hand, seems ideal for studying ionic transport in alluvial materials and soils.

The literature on diffusion presents information on diffusion of simple solutions. It would seem that geologists, at least, would be interested in diffusion in complex solutions since few simple solutions occur in nature. Anderson and Graf (1978) agree with this and state that acute problems of measuring the independent diffusion coefficients in systems of four or more components exist with current techniques. The frozen tube method may offer the means of studying the process of diffusion in natural waters.

6-3. Dissolved Metal Removal

The purpose of this study was to determine the feasibility of removing dissolved copper from a saturated porous medium using an electrochemical technique. The experimental work reported in Chapter 4 was performed in a single and specific environment. Future work should expand on this study by changing some of the variable parameters which define the environment.

6-3-1. Other Metals

It is known from the electroplating industry that many metals can be efficiently reduced from solution at the surface of an electrode. Some of the metals, such as lead, cadmium, and chromium, are toxic and pose a threat to the environment. I think it would be valuable, even from an academic standpoint, to pursue a project similar to this study using one of these metals as the solute. If someone desired to try the electrochemical technique in a field situation containing some metal other than copper, a laboratory test simulating field conditions would be essential.

6-3-2. Electrode Spacing

A study should be performed in which the distance between the anode and cathode is varied. In this study the distance was arbitrarily fixed at six inches for two reasons, equipment limitations and it produced useful results. If nothing is varied except the distance between the electrodes, the results should show some change because the electrical potential gradient will be varied. The electrical potential gradient is expressed as volts per unit length and it controls ionic mobility, which is expressed as velocity per unit of potential gradient, $\text{cm sec}^{-1}/\text{volt cm}^{-1}$.

An expanded study of electrode spacing should also be conducted in which electrode spacing is studied in conjunction with the movement of the fluid (Section 6-3-4). It may be possible that a greater velocity of groundwater could be tolerated if the anode and the cathode were placed farther apart.

6-3-3. Other Porous Media

Probably the single most valuable step beyond the work performed in this study would be to duplicate this work changing only the porous medium. One might use in place of the quartz sand, a standard clay or an actual soil. If a standard clay were used, one could investigate the effect of cation adsorption by the clay in view of all of the reactions taking place such as the change in pH between the electrodes. If a field test were anticipated, it would be essential to first conduct a frozen tube experiment using the actual soil from the field site.

6-3-4. Fluid Movement

All experimental work in this study was performed under conditions of a static fluid. The discussion of fluid movement in Section 5-2-2 produced only an estimate of the maximum allowable velocity of groundwater. In order to produce solid data on metal removal as a function of the velocity of the water, additional experiments should be run. Figure 6-1 shows a schematic of the type of apparatus that I would envision using. The input line could be connected to a pump which could accurately force a very low flow of fluid through the porous medium.

In order to estimate a fluid velocity to use as a starting point for these experiments, a frozen tube experiment should be conducted. The parameters of the frozen tube and its contents should be the same as those shown in Figure 5-1, except that the fluid will be stationary in the frozen tube experiment. The maximum

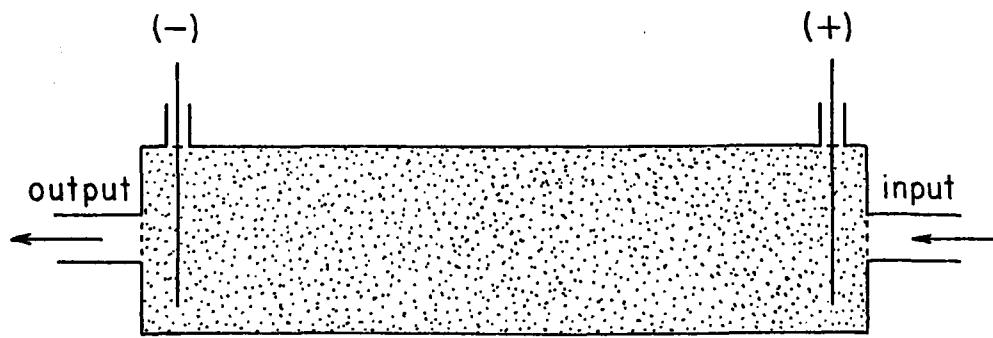


Figure 6-1. Apparatus for studying electrochemical removal of dissolved metal from solution as a function of the percolation velocity of the solution.

permissible velocity of the fluid can be estimated in the manner described in Section 5-2-2. The value of the apparent fluid velocity, also called percolation velocity, can be used to calculate the specific discharge of the porous medium (Bear, 1972, p. 121):

$$q = \Phi v_p \quad (6-1)$$

where q = specific discharge of the porous medium (cm/sec)

v_p = apparent velocity of fluid (cm/sec)

Φ = porosity of the porous medium (dimensionless).

The specific discharge of the porous medium is equal to the value which should be used for the discharge of the pump. From this starting point, the relationship between metal removal and percolation velocity could be studied but, most importantly, the maximum allowable fluid velocity could be determined.

6-4. Other Geochemical Phenomena

The frozen tube method of studying ionic transport may be ideally suited for studying some other geochemical phenomena not even approached in this study. Two ideas are listed here but this should not be construed as the end of the possibilities. Certainly a more adroit mind could expand this list considerably.

6-4-1. Dissolution of Solids

The dissolution of soluble minerals could be studied as a function of several rate controlling variables. The basis of the

idea is that dissolution as well as ionic transport would stop when the system was frozen in liquid nitrogen. Two types of systems could be examined, dissolution of a solid in a stagnant fluid and dissolution of a solid in a moving fluid. In the stagnant system the dissolved ions would be transported away from the solid only by diffusion. A system could be built similar to that shown in Figure 6-1, only without electrodes, to study dissolution of a mineral in a moving fluid. It would be important in any system to separate out the remaining solid from the rest of the system while it was still frozen.

6-4-2. Column Studies

Column studies are generally designed to study ion exchange and adsorption. Conventional column studies, however, only reveal an overall result. The knowledge and understanding of what is happening inside of the column could be greatly expanded using the frozen tube method. The processes in the column could all be halted at a given time by freezing. Slicing the column into sections while it was frozen could reveal any differences in reactions between the top and bottom of the column. The solution from the pore spaces of each section could be examined. The porous material from each section could be washed to find out what adsorbed ions are easily removed. Finally, the composition of the porous matrix itself could be analyzed for changes which resulted from the percolating solution.

6-5. Summary

I feel that this study made contributions in two areas: (1) the development of the frozen tube method as a new laboratory technique and (2) the proposal of the electrochemical technique for removing dissolved metals from a saturated porous medium as a possible environmental tool. If these contributions prove worthwhile, however, this study has just scratched the surface. There is a plethora of work which could be done along these lines. I have recorded my ideas for future work in this chapter. I hope that one of these ideas will spark some other researcher to prove (or disprove) the worth of this study.

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